A COMPARISON OF THREE METHODS USED FOR DETERMINING CHLORIDE IN ACID COPPER SULFATE PLATING BATH

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ABSTRACT

Monitoring of chloride concentration in acid copper suflate plating bath is vital due to its important role in the quality of copper deposition. In this study, three different analytical methods which include potentiometric titration, UV-Vis spectroscopy and ion chromatography were used to determine the chloride in an actual acid copper sulfate plating bath to investigate their respective analytical performances. From the Oneway Anova and Tukey-Kramer test conducted, it can be concluded that the results from these three methods are significant different, with ion chromatography method showing the greatest difference compared to the other two methods. Besides this, it is determined that potentiometric titration method has an excellent precision and accuracy, UV-Vis method is quite precise but less accurate, and IC method is the least precise and accurate. Taking account of other factors such as skill required, reagents required, sample preparation time, analysis time, cost per sample, maintenance cost and others, potentiometric titration method is the most ideal method to be used.

ABSTRAK

Pengawalan klorida dalam larutan penyaduran asid kuprum adalah sangat penting kerana peranannya dalam mengekalkan kualiti penyaduran kuprum. Dalam kajian ini, tiga kaedah analisis yang berbeza termasuk pentitratan potentiometrik, UV-Vis spektroskopi dan ion kromatografi telah digunakan untuk menentukan kepekatan klorida dalam satu larutan penyaduran asid kuprum untuk menyiasat prestasi analisis masing-masing. Daripada ujian Oneway Anova and Tukey-Kramer yang telah dijalankan, kita boleh membuat kesimpulan bahawa hasil daripada tiga kaedah tersebut adalah amat berbeza. Kaedah ion kromatografi menunjukkan perbezaan yang terbesar berbanding dengan dua kaedah lain. Di samping itu, kaedah pentitratan potentiometrik telah ditentukan mempunyai kejituan dan kepersisan yang amat baik, kaedah UV-Vis spektroskopi agak persis tetapi kurang jitu, dan kaedah ion kromatografi adalah kaedah yang paling kurang persis dan jitu. Mempertimbangkan faktor-faktor seperti kemahiran yang diperlukan, reagen yang diperlukan, masa penyediaan sampel, masa analisis, kos bagi setiap sampel, kos penyelenggaraan dan lain-lain, kaedah pentitratan potentiometrik merupakan kaedah yang paling sesuai digunakan.

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LIST OF ABBREVIATIONS

UV-Vis	Ultraviolet-visible
IC	Ion Chromatography
DI	Deionized
ppm	Part per million
No.	Number
Conc.	Concentration
Vol.	Volume

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CHAPTER 1

INTRODUCTION

1.1 Copper Electroplating

Electroplating is a process of electrodeposition of a thin and smooth metallic deposit over a conductive surface. Copper is one of the most common metal that found plated on plastics, printed wiring boards, zinc die castings, automotive bumpers, rotogravure rolls, electrorefining and electroforming with some of the examples shown in Figure 1.1. It is electroplated for numerous different decorative and engineering applications which require a wide range of mechanical and physical properties (Safranek, 1986). Due to its outstanding capability in covering minor imperfections of the base materials, copper plating has been widely used for undercoat. Copper is relatively inert in most of the common metal plating solutions, has a very high plating efficiency; thus providing excellent coverage on the plating parts, and lastly, its high electric conductive property also makes it an excellent choice for coating printed wiring boards or steel wires (Flott, 1996). Furthermore, copper plating is also very suitable for automotive parts which are constantly heated and cooled during their daily operations as the copper layers can serve as thermal expansion barriers by absorbing the stress produced when metals with different thermal coefficients undergo temperature changes (Snyder, 1991). Although copper is corrosion resistant, it is highly susceptible to staining and thus limiting it to be used as a decorative coating. In addition, it also forms a nobel-metal-base-metal couple that is prone to corrosion when being used as a coating for steel aluminium or zinc (Mohler, 1969).

Figure 1.1: Various copper plated parts

1.2 Acid Copper Sulfate Plating Bath

Some of the most commercially used copper plating systems include alkaline cyanide and pyrophosphate complex ion systems as well as acid sulfate and fluoborate simple ion systems. Among all, the acid sulfate system is the most widely used.

Copper deposit produced in cyanide solution is typically thin (<12.5 μm) and therefore it is not suitable for the deposition of relatively thick deposit in electroforming and other similar applications. Furthermore, due to the toxicity of cyanide solution and its associated waste treatment problems, most of the users are switching to other noncyanide solutions. Indeed, both pyrophosphate solution and fluoborate solution are also mostly replaced by sulfate solution due to its capability to provide comparable high current densities, cheaper, easier to control and less susceptible to impurities (Dini and Snyder, 2010).

Two major components in the highly conductive acid copper sulfate plating solution are copper sulfate and sulfuric acid which supply the ionized species. However,

the composition of the bath can be varied accordingly in order to achieve the targeted plating rate and the desired type of deposit. In some cases, some specialized additives are added to enhance the plating efficiencies such as throwing power, levelling effect, brightness and others. Compositions of some standard acid copper sulfate baths were shown in Table 1.1.

For most applications, the baths are operated at room temperature with mild agitation. To prevent immersion coatings and poor adhesion, the steel parts must be first cyanide copper- or nickel-plated in strike formulations before being plated in the baths. Zinc die castings and other acid sensitive metals must have sufficient deposit to prevent attack by the sulfuric acid. Phosphorized (0.02-0.08%), oxide-free, high-purity, rolled copper anode or copper anode nuggets in titanium baskets can be used. The anode current density should be maintained between 15-30 A/ft^2. Higher current densities will cause the anode to lose its black protective film which results rough deposits; whereas, lower current densities lead to build-up of copper sulfate, reducing the throwing power, and a thicker anode film reducing the conductivity of the anodes (Barauskas, 2013).

Table 1.1 Compositions of standard acid copper sulfate baths (Barauskas, 2013).

General Formulation	
Copper sulfate	195-248 g/L
Sulfuric acid	30-75 g/L
Chloride	50-120 ppm
Current density	20-100 A/ft^2
Semibright plating (Clifton-Phillips)	
Copper sulfate	248 g/L
Sulfuric acid	11 g/L
Chloride	50-120 ppm
Thiourea	0.00075 g/L
Wetting agent	0.2 g/L

Bright Plating (Beaver)	
Copper sulfate	210 g/L
Sulfuric acid	60 g/L
Chloride	50-120 ppm
Thiourea	0.01 g/L
Dextrin	0.01 g/L
Bright Plating (Clifton-Phillips)	
Copper sulfate	199 g/L
Sulfuric acid	30 g/L
Chloride	50-120 ppm
Thiourea	0.0375 g/L
Molasses	0.75 g/L

1.3 Mechanism of Copper Electroplating Process

The mechanism of copper electroplating can be explained with the help of Figure 1.2 which shows a wafer coated with a thin electrically conductive layer of seed copper that is immersed in a copper sulfate solution. When current is applied, the electrical energy provided is converted to chemical energy by decomposition, dividing elements into positive and negative charged ions. The positively charged Cu^{2+} ions in the solution are then attracted and moved towards the cathode surface and deposited onto it. The consumed Cu^{2+} ions will then be replenished from the solid copper anode. This process can be described by the equations:

$$\text{Cathode: } Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)}$$

$$\text{Anode: } Cu_{(s)} - 2e^- \rightarrow Cu^{2+}_{(aq)}$$

The first stage of the electrodeposition of copper depends on the deposition rate, the surface nature of the substrate and the deposition technique employed (Brande and Winand, 1993); while the final stage in the growth of copper deposit involves an

equilibrium between the dissolution and the precipitation of copper electrochemically (Anderson *et al*., 1994). The properties of the resulted copper deposits are generally influenced by the concentrations of copper salts, additives, free acid, operating temperature, cathode current density and the nature and degree of agitation.

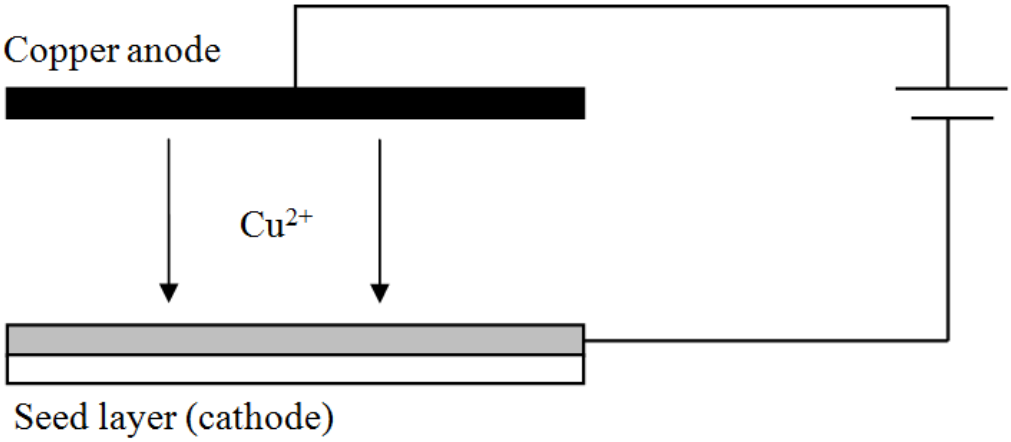


Figure 1.2: A copper electroplating system

1.4 Functions of Acid Copper Sulfate Plating Solution Constituents

1.4.1 Copper Sulfate

The major function of copper sulfate is to provide the copper ion required for electroplating. Its concentration is not particular important, however the resistivity of the solution tends to be greater with the increase of the concentration. Besides this, the cathode polarization increases slightly when the concentration of copper sulfate increases above 250 g/L while the cathode efficiency decreases when the concentration drops below 60 g/L (Dini and Snyder, 2010). The solubility of copper sulfate in the solution decreases when the concentration of sulfuric acid increases. It is not recommended to maintain the concentration of copper sulfate too near to the solubility limit as any increase in copper sulfate content or decrease in bath temperature can lead to the formation of copper sulfate crystals which will affect the plating quality.

1.4.2 Sulfuric Acid

Copper can be deposited well from an acid-free sulfate solution only at very low cathode current densities. At higher current densities, the copper deposit is spongy due to the increase of pH in the cathode film, leading to the formation of occluded salts in the deposit. This can be solved by adding suitable amount of sulfuric acid, the free acid helps to improve plate quality at higher current densities, improve anode corrosion, increase solution conductivity, prevent the precipitation of basic compounds and lower both anode and cathode polarizations (Mohler, 1969). Throwing power of the solution can be increased greatly by maintaining the weight ratio of copper metal to sulfuric acid at less than 1:10. This is very useful for plating high aspect ratio printed circuit boards, however the lower copper content decreases the allowable plating current densities, thus leading to a longer plating time in order to achieve the copper deposit thickness desired (Barauskas, 2013). On the other hand, excess amount of sulfuric acid will greatly increase the cathodic overpotential and introduce a smaller ratio of level plane of electrodeposits, leading to the formation of nodular precipitates (Fukunaka *et al*., 1998).

1.4.3 Chloride

The presence of chloride ions in the bright and high throw formulations acid copper sulfate plating solution plays an important role in reducing anode polarization and eliminating the striated deposits in high current density areas. It is crucial to control the concentration of chloride ion between 60 to 80 ppm. If the concentration of chloride ion falls below 30 ppm, copper deposits formed will be dull, striated, coarse and step (skip) plated. On the other hand, if the concentration of chloride ion exceeds 120 ppm, copper deposits formed will be coarse grained and dull, and polarization of anodes will occur, stopping the plating process (Duffek, 1996). The chloride ion generally

influences the surface appearance, structure, microhardness, crystallographic orientation, and internal stress of the deposits. A minimum amount of chloride is useful in improving the ductility of copper deposits from two different proprietary copper plating solutions, the elongations of each deposits were found to be greatly improved with an introduction of 10 ppm of chloride (Anderson et al., 1985). Chloride ion also proved to be the most effective halides over a wide range of concentration (40-150 ppm) in eliminating the internal stress of copper deposits and it also possess synergistic effect over some brightening additives that normally used (Gana *et al*., 1979). Small amount of chloride ions also help to accelerate the deposition rate of copper by acting as binding sites for surfactants such as polyethylene glycol to the electrode surface (Melnicki, 1988). However, excess amount of chloride ion can cause the precipitation of insoluble copper chlorides at the anode surface, interrupting the electrodeposition process (Goodenough and Whitlaw, 1989).

1.4.4 Additives

An extensive list of additives has been used in the acid copper sulfate plating solution for brightening, hardening, grain refining, surface smoothing, increasing the limiting current density and reducing trees have been reported in the literature. Some examples of the additives are thiourea which acts as a brightener; gelatin and glue which help to reduce treeing, refine grain size and harden deposits; ethanol which is added to improve throwing power; potassium aluminium sulfate which can reduce the nodular precipitates and increase the conductivity of the plating bath; molasses and orthophenolsulfonic acid which are used to achieve hard and tough deposits (Rodgers, 1959). Many of the latest commercially available additives are made up of three chemicals designated as carriers which are typically polyalkyene glycol type polymers

with a molecular weight around 2000, leveller which are typically alkane surfactants containing sulfonic acids and amine or amide functionalities, and lastly brighteners which are typically propane sulfonic acids that are derivatized with surface active groups containing pendant sulfur atoms (Reid, 1987). However, it is very important to evaluate the use of a particular additive for each application to avoid any undesirable characteristics. For examples, gelatin may induce porosity or organic inclusion (Marie and Jacquet, 1929) and thiourea can cause nodulation, an effect always associated with a large increase in overpotential, >100 mV (Suarez and Olson, 1992).

1.5 Effects of Impurities in Acid Copper Sulfate Plating Solution

Various impurities may be introduced into the acid copper sulfate plating solution throughout the plating process in many ways. Their existences in the bath cause different type of defects to the copper deposits. Following are some of the most common impurities found.

1.5.1 Metallic Ions

Acid copper sulfate plating solution is less susceptible to contamination by metallic impurities than other plating solutions. Many metallic ions such as iron, nickel, zinc and others are introduced regularly by carryover, dissolution of impurities in the anode and dissolution of the basis metal. They accumulate in the solution as the conditions are not suitable for effecting co-deposition with copper. Some common metallic contaminants and their effects are as follows: nickel and iron (>1000 ppm) may reduce the conductivity of the solution and throwing power. Cadmium and nickel (>500 ppm) can cause immersion deposit, polarization of the anode during idle time and tie up

of chloride ions (Barauskas, 2013). Lead tends to precipitate and cause micro-roughness. Hexavalent chromium at very low concentrations (~5 ppm) can cause darkening and blistering of copper deposits and lead to poor adhesion of subsequent nickel deposits. Hexavalent chromium can be reduced to trivalent chromium by adding sodium hydrosulfite, however it must be added regularly as the trivalent chromium will slowly reoxidized to hexavalent chromium at the anode (Rodgers, 1959). Arsenic and antimony in concentrations of 20-100 ppm and 10-80 ppm respectively may cause rough and brittle deposits. Additives such as gelatin or tannin can be added in order to overcome these problems (Hospadaruk and Winkler, 1953). Similar to arsenic and antimony, the presence of bismuth in the solution can cause granular deposits. In addition, antimony and bismuth also tend to form insoluble complex compounds with arsenate (Mosher, 1960).

1.5.2 Organic Impurities

Organic impurities originate primarily from the decomposition of organic additives and partially from the leaching of elastometric tank linings. Significant organic contamination is indicated by a green coloration of the bath. They are usually removed by filtration by the activated carbon. However, for some highly contaminated baths, potassium permanganate, hydrogen peroxide, or even bleach may be necessary in order to break down the organic compounds so that they can be removed effectively with activated carbon. The activated carbon must be designed for use in high acid baths, otherwise itself may be a source of contamination or have no effect (Barauskas, 2013).

1.5.3 Nitrate

Nitrates are reduced to ammonia at the cathode in acid copper sulfate plating solution. The ammonia generated will then reduce the sulfate ions in the solution, leading to grain-coarsening problem. It can be simply solved by heating the solution or adding oxidizing agents. However, oxidizing agents such as hydrogen peroxide or potassium permanganate may well reduce the throwing power (Dini and Snyder, 2010).

1.5.4 Chloride

Excess amount of chloride ions are usually introduced into the acid copper sulfate plating solution when tap water which contains a high chloride content is used. High concentration of chloride in the solution may cause treeing and nodular deposits. It can be removed by precipitation with silver sulfate, zinc dust or by treating the solution with activated carbon (Rodgers, 1959).

1.6 Objective

The performance of an acid copper sulfate plating is greatly depends on the bath condition, where the concentration of chloride ions has been identified one of the key factors. In this regards, the quantitative analysis of the chloride ions in the plating solution is crucial in quality assurance and quality control. The main objective of this study is to evaluate and to compare the analytical performance of three different methods which includes potentiometric titration, UV-Vis spectroscopy and ion chromatography (IC) in the determination of chloride in acid copper sulfate plating bath.

CHAPTER 2

LITERATURE REVIEW

2.1 Introduction

Titration has been the most widely used method in electroplating industry to determine the chloride in acid copper sulfate plating solution because it is easy to conduct, fast and relatively cheap comparing to other methods. However, the precision achieved by manual titration depends mainly on the chemist's skill and ability for perception of different colours. That is why most of the laboratories prefer potentiometric titration nowadays as it employs potentiometric sensors to determine the endpoint, replacing the colour indicators and thus increasing precision and accuracy of results. On the other hand, alternative methods such as UV-Vis spectroscopy and ion-chromatography are not so popular due to the relatively tedious sample preparation steps, longer analysis time and higher cost in instrument maintenance.

It is generally agreed that various contaminants are accumulated in the acid copper sulfate plating bath gradually throughout the plating operations. Due to the high cost of replacing or treating it regularly, most of the users will just continue to replenish and use it until it is no longer able to provide the desired qualities. This raises a concern that the build-up may bring about additional uncertainty in the chloride concentration depends on the analytical method that was applied. In this study, the above mentioned analytical methods were used to determine the chloride in an actual acid copper sulfate plating bath that had been operated for more than one year.

2.2 Titration Method

Titration is an analytical technique which allows the quantitative determination of a specific analyte dissolved in a sample based on a complete chemical reaction between the analyte and a titrant of known concentration. To determine chloride, argentometric titration which is a type of titration based on the precipitation of silver compounds is normally used. It can be generally divided into three different types which are Mohr, Volhard and Fajans Method.

2.2.1 Argentometric Titration - Mohr Method

This method uses potassium chromate which is yellow colour as an indicator in the titration of chloride ions with silver nitrate solution. The added silver nitrate solution will first react with the chloride ions in the sample solution to form white precipitate of silver chloride.

$$Ag_{(aq)}^{+} + Cl_{(aq)}^{-} \rightarrow AgCl_{(s)}$$

The endpoint is then indicated when all the chloride ions had been precipitated and additional chloride ions reacted with the chromate ions of the indicator to form red-brown precipitate of silver chromate.

$$2Ag_{(aq)}^{+} + CrO_4^{2-}{}_{(aq)} \rightarrow Ag_2CrO_{4\,(s)}$$

This method requires the pH of the sample solutions have to be adjusted to near neutral (7 to 10) because at higher pH, brown silver hydroxide precipitate may form and mask the endpoint while at lower pH, most of the chromate ions will be protonated to chromic acid form, leaving too little chromate ions to form the red-brown precipitate of silver chromate at the equivalence point, thus affecting the accuracy (Kraemer and

Stamm, 1924). The change of colour from yellow to red-brown at the endpoint happens gradually and an additional excess of the silver nitrate is normally needed to form enough silver chromate to be seen over the heavy white precipitate of silver chloride (Clarke, 1957). This will introduce a positive systematic error, especially for sample solutions containing low concentration of chloride or have deep colour such as the sample of this study, acid copper sulfate plating solution.

2.2.2 Argentometric Titration - Volhard Method

In this method, an excess amount of silver nitrate will be added into the sample solution to react with the chloride ions to form white precipitate of silver chloride.

$$Ag_{(aq)}^{+} + Cl_{(aq)}^{-} \rightarrow AgCl_{(s)}$$

The unreacted silver ions are then titrated with a standard solution of potassium thiocyanate in the presence of ferric ammonium sulfate solution (which acts as an indicator). The titrate remains pale yellow as the free silver ions react with thiocyanate ions to form silver thiocyanate precipitate.

$$AgSCN_{(s)} \rightarrow Ag^{+}_{(aq)} + SCN^{-}_{(aq)}$$

After all the free silver ions had been completely reacted with thiocyanate ions, the first excess thiocyanate ion will react with the ferric ions of the indicator to form the red ferrithiocyanate complex, indicating the endpoint.

$$Fe^{3+}_{(aq)} + SCN^{-}_{(aq)} \rightarrow FeSCN^{2+}_{(aq)}$$

The concentration of chloride ion in the sample solution is determined by subtracting the titration findings of the moles of silver ions that reacted with the thiocyanate ions from the total moles of silver nitrate solution that added. However, due

to the fact that silver thiocyanate is less soluble than silver chloride, the thiocyanate ions tend to react with the silver chloride precipitate, releasing the chloride ions and thus contributing to error.

$$AgCl_{(s)} + SCN^-_{(aq)} \rightarrow AgSCN_{(s)} + Cl^-_{(aq)}$$

In order to eliminate this error, nitrobenzene can be added in order to coat the colloidal silver chloride precipitate, preventing them from reacting with thiocyanate ions. However, the method is not recommended as nitrobenzene is carcinogenic.

Another way is simply removing the silver chloride precipitate by filtration. However, the colloidal silver chloride precipitates are too small to be completely removed by filtration and they have a very high surface area on which a significant amount of silver ions may also be adsorbed onto. These silver ions will lost along with the silver chloride, thus contributing to the error in the amount of excess free silver ions determined in the following titration. The coagulation of these small precipitates into larger and more readily filterable ones can be facilitated by addition of some inert electrolytes such as nitric acid. This is to increase the ionic strength of the solution which in turn helps to minimize the effect of the repulsive forces between those positively charged colloidal silver chloride precipitates, allowing them to move closer to each other so as to form larger precipitate. In addition, the protons from nitric acid can displace the silver ions that adsorbed, thus minimize the error due to the loss of silver ions through filtration (Ernest *et al*., 1950).

Volhard method is quite suitable for determining the chloride content in acid copper sulfate plating solution as the highly acidic environment helps to eliminate interferences from carbonate, oxalate and arsenate (Skoog *et al*., 2004). However, similar to Mohr method, Volhard method also faces the same difficulty in judging the real endpoint due to the masking of deep blue colour of acid copper sulfate plating

solution. Moreover, it is generally more time consuming due to the additional filtration process to remove the silver chloride precipitate.

2.2.3 Argentometric Titration - Fajans Method

Different from both the argentometric methods discussed above, Fajans method employs an adsorption indicator such as dichlorofluorescein which is a weakly acidic dye that exists in ionized form in the solution. Its principle works on the fact that colloidal silver chloride precipitates tends to adsorb silver ions or chloride ions whichever happens to be in excess as illustrated in Figure 2.1. Before the equivalence point of the titration, the chloride ions are in excess and hence they will form a primary adsorption layer on the surface of the silver chloride precipitates. These silver chloride precipitates are now negatively charged surface and repel each other. As the indicator ions are also negatively charged, they will also be kept away from the surface of these silver chloride precipitates. Yet, these negatively charged precipitates can attract the available cations in the solution, forming a weakly bound secondary adsorption. On the other hand, after the equivalence point, silver ions become in excess and hence the silver ions will replace the chloride ions as the primary layer. This causes the precipitates to be positively charged and capable of attracting the indicator anions to form the secondary adsorption layer. Such interactions between adsorbed dichlorofluorescein ions and adsorbed silver ions result the dichlorofluorescein to change from yellow-green colour to pink, indicating the endpoint (Skoog *et al*., 2004).

This method is also not suitable for the determination of chloride in acid copper sulfate plating solution. The presence of high concentration of ionic constituents in acid copper sulfate plating solution cause the silver chloride precipitates to coagulate together. This decreases the overall surface area and thus the indicator colour transition

is almost invisible. It is true that starch can be added to prevent such coagulation; however, the colour change at the endpoint still be masked by the deep blue colour of the sample solution. Furthermore, the high amount of hydrogen ions that associated with the acidic copper sulfate plating solution will react with the negatively charged indicator ions, thus greatly decrease the concentration of free indicator ions and limiting its adsorption on the silver chloride precipitates. Above pH 9, the precipitation of silver hydroxide may occur. To sum up, such adsorption indicators are only appropriate for pH ranges from 5 to 9 (Harris, 2003).

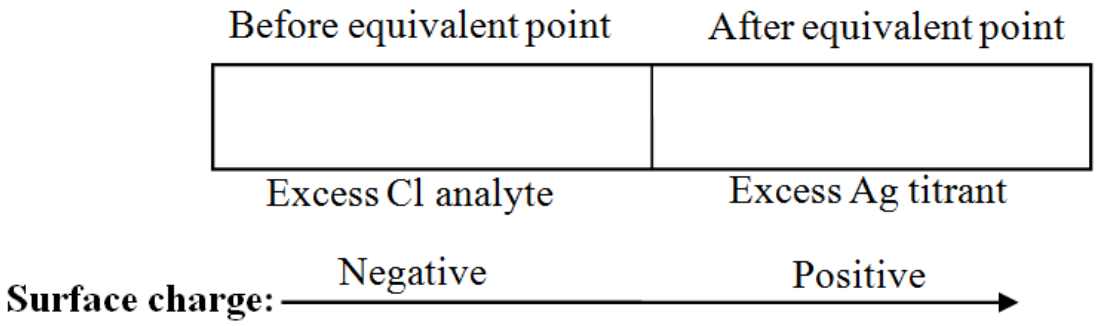


Figure 2.1: The process of Fajans titration

2.2.4 Potentiometric Titration Method

One of the major problems encountered in determining the concentration of chloride in acid copper sulfate plating solution by using those argentometric titration methods discussed above is the difficulty in judging the colour change at the endpoint due to the deep blue colour of the solution. This issue will greatly reduce the accuracy and precision of such methods. This problem can be overcome by using potentiometric titration method which determines the endpoint potentiometrically using an indicator electrode. The general setup of a potentiometric titration system is shown in Figure 2.2. In case of argentometric titration of chloride ions, the electrochemical cell can be written as:

$$\text{Reference} \parallel Ag^{+}, Cl^{-}, AgCl_{(s)} \mid Ag_{(s)}$$

The reference electrode usually contains a liquid junction that completes the electrical circuit. The potential of this cell can be written as

$$E_{cell} = E_{ind} - E_{ref}$$

where E_{ind} is the half-cell potential at the indicator electrode due to the species in the sample solution and E_{ref} is the half-cell potential at the reference electrode which always stays constant during the titration. The changes in the cell potential correspond to the variations in the concentrations of species in a sample solution.

At the indicator electrode, the dissolved silver ions tend to be reduced to silver metal.

$$Ag^{+} + e^{-} \leftrightarrow Ag_{(s)}$$

The potential of this half-reaction will depend on the concentration or the activity of silver ions present in the sample solution as described by the Nerst equation:

$$E_{ind} = E^{o}_{ind} + \frac{2.303.\ R\ .T}{Zi\ .\ F}\ .\ \log a_i = E^{o}_{ind} + E_N\ .\ \log a_i$$

where E_{ind} = Measured potential between indicator and reference electrode

E^{o}_{ind} = Standard potential of the measuring assembly

R = Gas constant (8.31441 $JK^{-1}mol^{-1}$)

T = Absolute temperature in K

z_i = Charge of measuring ion i (including sign), +1

F = Faraday constant (96484.56 $Cmol^{-1}$)

a_i = Activity of measuring ion, Ag^+

E_N = Nernst Slope

The Nernst slope, E_N specifies the theoretical electrode slope which corresponding to the potential change caused by the change in activity of measuring ions, a_i by the factor of ten. It depends on the temperature and charge of the measuring ion, z_i. It is 59.16 mV at 25 ^oC for univalent positively charged ions (Haider, 2004). As the measure potential is directly proportional to the concentration of silver ions, a plot of E_{cell} versus the amount of silver nitrate added will produce a sigmoidal titration curve (blue line) as shown in Figure 2.3. The first derivative of the titration curve (red line) shows a peak whose maximum indicates the endpoint of the titration.

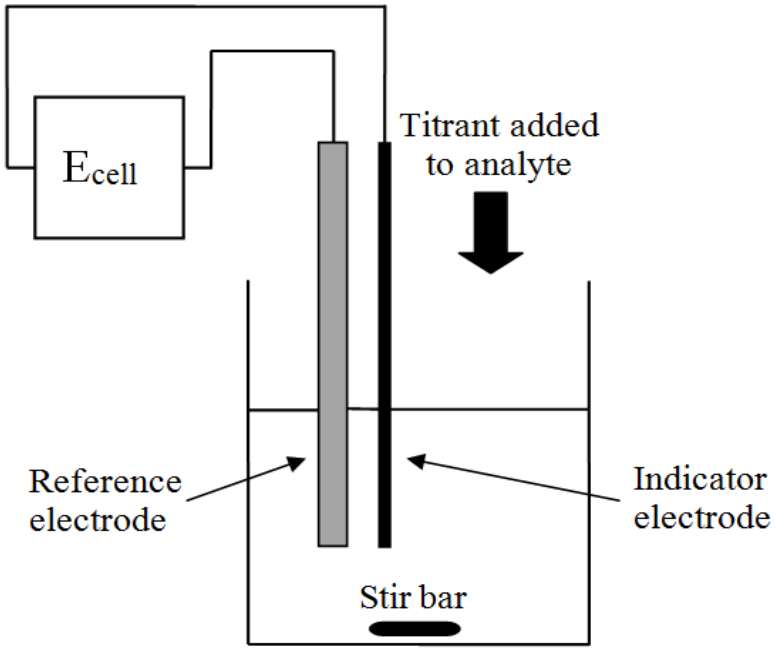


Figure 2.2: General setup of a potentiometric titration system

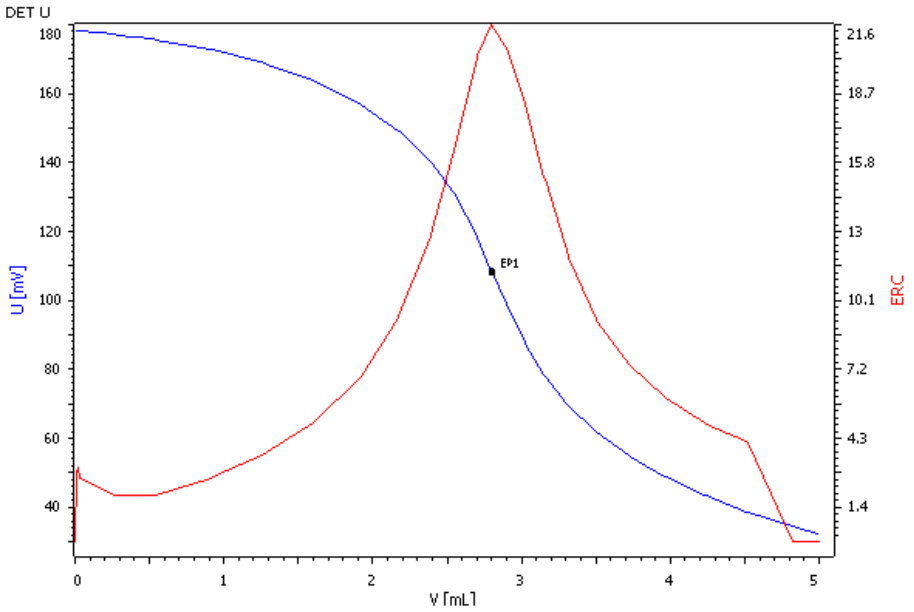


Figure 2.3: Potentiometric titration curve

Another major problem encountered in argentometric titration methods is that silver nitrate can form sparingly soluble precipitates with many other interfering anions, contributing to determination error. However, potentiometric titration method will not have this problem as the titration curve can show several equivalence points corresponding to different anions present in the sample solution. The anions that forms the least soluble compound with silver ions can be outlined and it is indicated as the first equivalence point in the resulting titration curve. For example, in a simultaneous determination of bromide and chloride using potentiometric titration method, two equivalence points are obtained; the first equivalence point corresponds to the bromide content while the difference between the second and the first equivalence point corresponds to the chloride content as shown in Figure 2.4. As a rule of thumb, for such quantitative separation of anion mixtures is that the solubilities of the corresponding silver compounds must differ as much as possible. In some cases, barium acetate or acetone can be added to facilitate the separation. Besides this, those anions also should not have great differences in term of their concentrations (Metrohm - application bulletin 130/ 3e).

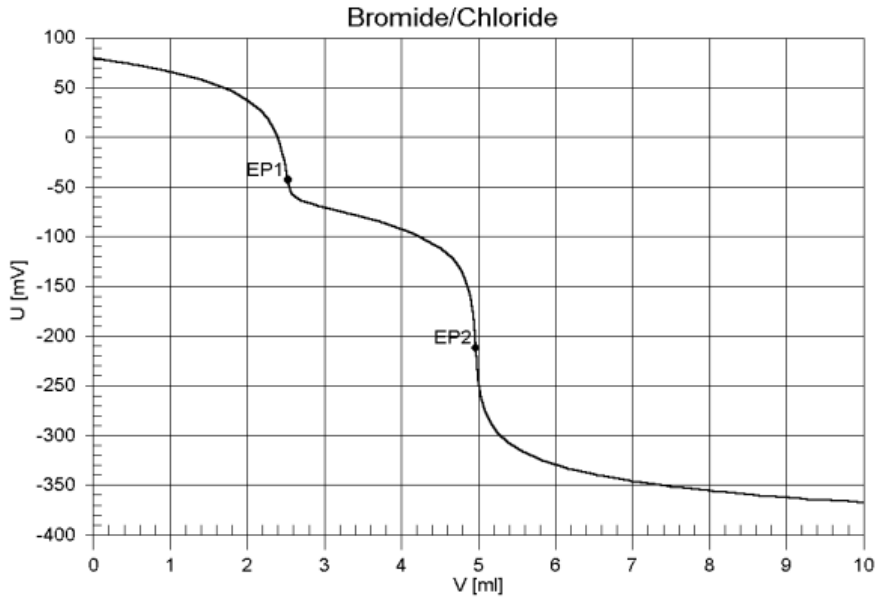


Figure 2.4: Titration curve for simultaneous determination of bromide and chloride (Metrohm - application bulletin 27/ 2e)

In order to minimize the interferences, any cyanide, sulfides and thiosulfates present in the sample solution can be removed by mean of oxidation with hydrogen peroxide which itself must also be removed prior to the titration. Besides this, a protective colloid, 0.2% polyvinyl alcohol solution can be added into the sample solution to prevent coagulation of the silver chloride precipitates and keeping the electrode surface practically free from any deposits. Bright silver electrode is normally preferred for such application as it has no diaphragm (eliminate the blockage problem) and no need to refill any electrolyte. Its glass membrane acts as a reference electron which is capable to provide a constant potential in sample solution with a constant pH value (Gros, n.d.).

2.3 UV-Vis Spectroscopy Method

It is not possible to determine the chloride content directly using this technique due to the lack of a characteristic absorption band of chloride in the UV-Vis range (190-820 nm). Several indirect methods have been reported in the literature. Iwasaki *et al*., (1952) first introduced a method which involves the use of mercury thiocyanate and iron(III) ion, that capable to determine the chloride ion in the concentration range of 0.1-20 ppm. This method works on the principle that the chloride ions react with mercury thiocyanate, releasing an equivalent amount of thiocyanate ions, followed by a reaction with the iron(III) ions to form an orange colour thiocyanate-iron ion complex which can be determined photometrically at 460 nm.

$$2Cl^- + Hg(CNS)_2 \leftrightarrow HgCl_2 + 2CNS^-$$

$$4Cl^- + Hg(CNS)_2 \leftrightarrow HgCl_4^{2-} + 2CNS^-$$

$$CNS^- + Fe^{3+} \leftrightarrow Fe(CNS)^{2+}$$

However, this method provides a low sensitivity and low linearity. Tomonari (1962) solved this problem by changing the nitric acid to perchloric acid and iron(III) alum to iron(III) perchlorate. However, the method proposed required more complicated and tedious preparation and treatment procedures of reagents. Through a series of investigations on the influence of each reagents in different concentrations conducted by Yoshinaga and Ohta (1990), they claimed that a higher linearity and better sensitivity can be obtained just with higher concentrations of iron(III) alum (150-300 g/L in 6M HNO_3, 2 mL) and mercury thiocyanate (9 g/L in MeOH, 2 mL, or 4 g/L in MeOH, 4 mL). This method suffers interference from bromide, iodide, cyanide, thiosulfate and nitrite.

Another indirect method had been described by Barney II and Bertolacini (1957). In this method, the chloride ions reacts with mercuric chloranilate to release reddish purple acid chloranilate ions which are then determined photometrically at 530 nm.

$$HgC_6Cl_2O_4 + 2Cl^- + H^+ \leftrightarrow HgCl_2 + HC_6Cl_2O_4^-$$

Methyl cellosolve is added to lower the solubility of mercuric chloranilate and to suppress the dissociation of mercuric chloride and nitric acid to obtain maximum absorbance. Interfering cations can be removed with ion exchange resins but anions such as bromide, iodide, iodate, thiocyanate, fluoride and phosphate can interfere. In another study conducted by Kramer *et al*., (1994) on above mentioned method, it was reported that there are another two absorption maximum located at 332 nm and at about 325 nm, which appears as significant shoulder of the main peak for sample solutions with pH above 3.5. They found that lowering the pH further from 2 to 1.5 shifts the absorption maximum from 332 to 306 nm. The absorption maximum finally shifted further from 306 to 302 nm and the maximum at 530 nm will disappear if the pH falls below 1. Both the chloranilate and ferric thiocyanate methods are essentially equivalent in accuracy, precision and ease of operation. Interferences from cations and anions are also almost the same. However, the ferric thiocyanate method is slightly more sensitive and a correction must be done for chloride in the ferric alum used, whereas there is no need for correction in the chloranilate method.

Determination of chloride ion can also be done by further subjecting the soluble mercuric chloride to a complexing agent that in turn to form a water soluble absorbing species. In a study done by Humphrey and Hinze (1973), they found that phenolphthalein complexone (PPC) and xylenol orange (XO) can react with mercuric chloride in pH 11 to form $Hg(PPC)_2$ and in pH 7 to form $HgCl_2$-XO complexes respectively. The $Hg(PPC)_2$ complex has an absorption maximum at 568 nm with a

molar absorptivity of about 40000. The absorbance decreases with increase of cyanide, iodide and thiosulfate ions but did not change with bromide, chloride, or thiocyanate ions. On the other hand, the $HgCl_2$-XO complex has an absorption maximum at 588 nm with a molar absorptivity of about 24000. This xylenol orange method fails to provide a good linearity for calibration curve. Besides this, most metal ions present in the sample solution must be removed prior to the development of colour as xylenol orange tends to form colour complexes with many other metal ions. In addition, it is also expected to experience about the same anion interferences as with the use of phenolphthalein complexone.

It seems like these spectrometric methods are not so appropriate for direct determination of chloride content in the acid copper sulfate plating solution. This is due to the possible interferences from high concentration of sulfate, metal contaminants, numerous different kind of organic additives, deep colour and highly acidic condition of the solution. All these possible interferences must be taken into account to ensure the accuracy and precision of the methods.

2.4 Ion Chromatography Method

IC method has been used widely in monitoring the concentration of certain constituents of the plating solutions. Its biggest advantage compared to other methods is its ability to separate, identify and quantitate simultaneously low concentrations of several electroactive species. The determination of chloride content in acid copper sulfate solution using IC had been demonstrated in Dionex application note 143. In this IC method, the IonPac AS 15 column anion exchange column is used as it has sufficient capacity for the high-sulfate matrix and strong retention for sulfate, thus facilitating the separation of chloride peak from the sulfate peak (Figure 2.5). This method has been proved to be able to provide reliable result for over 500 injections (Dionex - application update 143).

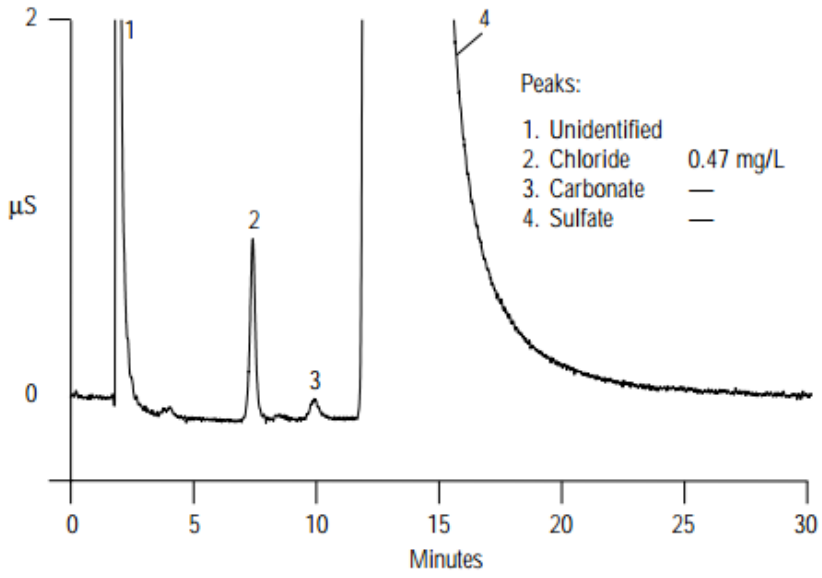
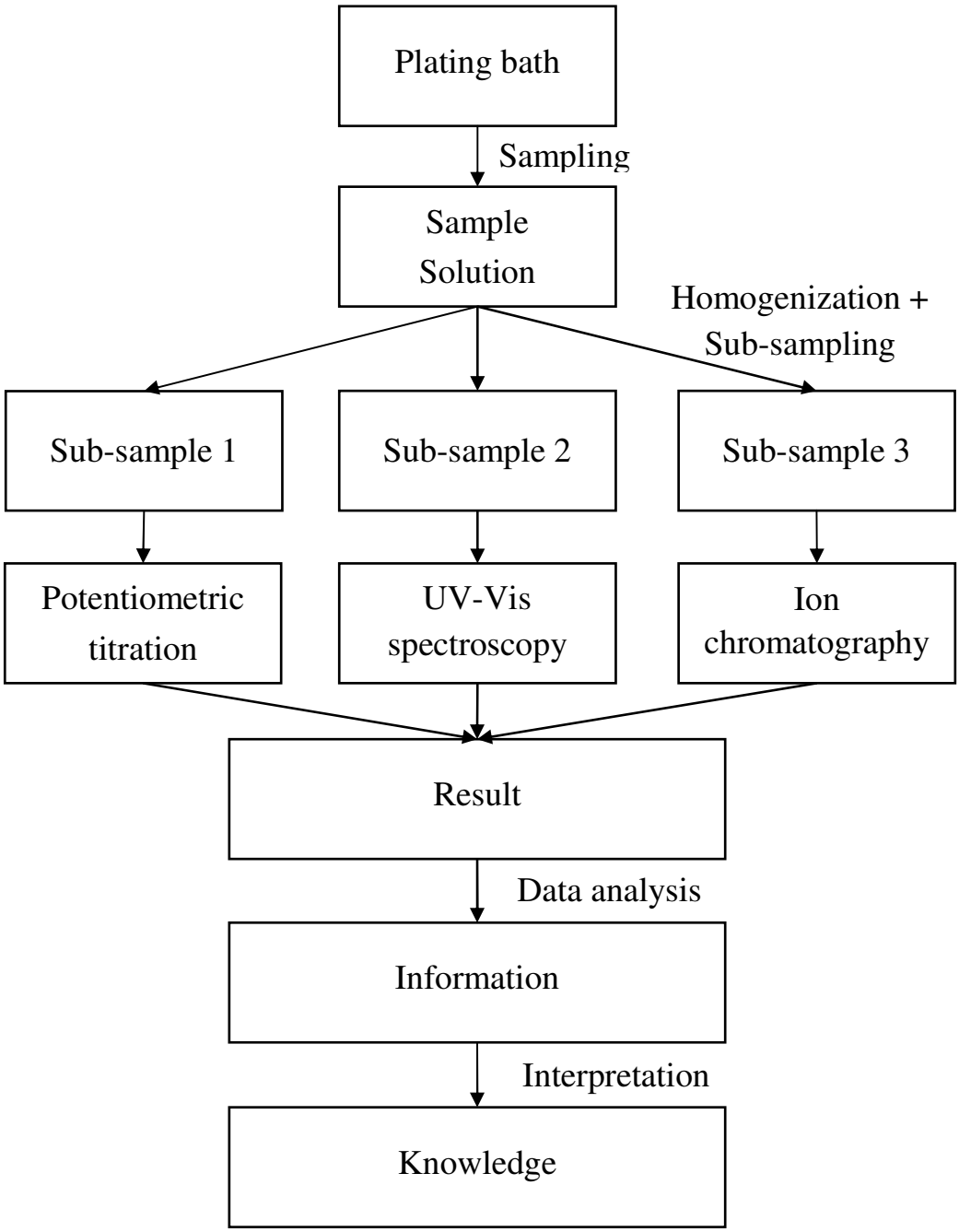


Figure 2.5: Chromatogram of determination of chloride in acid copper sulfate solution (Dionex - application update 143)

CHAPTER 3

METHODOLOGY

3.1 Workflow of Chloride Determination in Acid Copper Sulfate Bath



3.2 Sampling

Acid copper sulfate plating solutions were sampled from one of the Atotech's customer who uses it for plating motorcycle gear box cover. The samples were agitated for some time before sampling, as to ensure its homogeneity and exclude any sludge at the bottom of the bath.

3.3 Chemicals

All commercially available chemicals listed in Table 3.1 were used as received without any further treatments unless stated. Type 1 deionized water (18.2 MΩ-cm) was obtained from a Barnstead Easypure II water purification system.

Table 3.1: List of chemicals

Chemical	Company
• 37% Fuming hydrochloric acid • 0.1 M Silver nitrate volumetric solution • 1000 mg/L Chloride standard • Reagent grade ethylene glycol • Sodium chloride 99.99 Suprapur®	Merck (Germany)
• Potassium hydroxide eluent	Dionex (US)

3.4 Potentiometric Titration Analysis Procedures

3.4.1 Preparation of Standard NaCl Solution

The high purity NaCl was first dried overnight in a drying oven at 140 ^{o}C and left to cool in a desiccator for at least 2 hours. Approximate 60 mg of NaCl was weighted, transferred into a 100 ± 0.1 mL volumetric flask and top up to the mark with deionized water. The solution was shaken vigorously to fully dissolve all the NaCl solids.

3.4.2 Preparation and Standardization of 0.01 M $AgNO_3$ Solution

0.01 M $AgNO_3$ was prepared by topping up 100 mL of 0.1 M $AgNO_3$ volumetric solution with deionized water in a 1 L volumetric flask. Due to its light-sensitive property, it was stored in an amber glass bottle. As it is obvious that $AgNO_3$ degrades gradually over time, it was standardized with standard NaCl solution. This is to determine its real strength (titer), eliminating any possible errors due to the purity of titrant. For standardization, 10.00 ± 0.06 mL of the standard NaCl solution (equivalent to approximate 6 mg) was pipetted into a 100 mL titration beaker and mixed with 50 mL of deionized water. After adding in 1 mL of 2 M nitric acid solution, the solution was titrated with 0.01 M $AgNO_3$ until first endpoint using an automatic titrator. As 1 mL of 0.01 M $AgNO_3$ solution is equivalents to 0.5844 mg of NaCl, the titer can be adjusted using the following equation:

$$\text{Titer} = \frac{\text{Weight of NaCl (mg)}}{0.5844 \text{ x Vol. of 0.01 M } AgNO_3 \text{ consumed up to the endpoint (mL)}}$$

The temperature of the solution was remained constant during the titrations. The mean titer was determined triplicates of 3 individual standard NaCl solutions. This value was stored automatically in the automatic titrator system for calculating the chloride content in the consequent titration of the acid copper sulfate sample solutions.

3.4.3 Sample Preparation and Chloride Determination

50 mL of acid copper sulfate solution was pipetted into a 100 mL titration beaker and mixed with 20 mL of deionized water. The sample solution was then titrated with 0.01 M $AgNO_3$ until first endpoint using an automatic titrator. As 1 mL of 0.01 M $AgNO_3$ solution is equal to 0.3544 mg of chloride, the chloride content can be determined using the following equation:

$$\text{Chloride (mg/L)} = \frac{\text{Vol. of 0.01 M } AgNO_3 \text{ consumed up to the endpoint (mL)} \times 0.3544 \times 1000 \times \text{titer}}{\text{Sample volume (mL)}}$$

10 replicates were conducted to get a mean value.

3.4.4 Preparation and Determination of Spiked Sample

2.50 ± 0.06 mL of 1000 mg/L chloride standard solution and 47.5 mL of acid copper sulfate solution were pipetted into a 100 mL titration beaker and mixed with 20 mL of deionized water. The spike sample solution was then titrated with 0.01 M $AgNO_3$ until first endpoint using an automatic titrator. The chloride content was determined using the same equation stated in section 3.4.3. 10 replicates were conducted to get a mean value.

3.4.5 Instrumentation

The titrations of acid copper sulfate sample solutions with 0.01 M $AgNO_3$ to determine their chloride contents were performed using a Metrohm 905 Titrando equipped with an Ag/ AgCl electrode with AgCl coating. The endpoints were determined potentiometrically without the need of visual indication. The instrument's operating settings were shown in Table 3.2 below.

Table 3.2: Operating settings of Metrohm 905 Titrando

Parameter	Setting
Titration Parameters	
Measuring point density	4
Minimum increasement	10 µL
Dosing rate	Max. mL/min
Signal drift	30 mV/min
Minimum waiting time	0 s
Maximum waiting time	32 s
Temperature	25 ^{o}C
Stop Conditions	
Stop volume	30 mL
Stop potential	Off mV
Stop endpoint	1
Volume after endpoint	4 mL
Stop time	Off s
Filling rate	Max. mL/min
Evaluation	
Endpoint criterion	15
Endpoint recognition	Greatest

3.4.5.1 Coating of Ag/ AgCl Electrode

The Ag electrode was first thoroughly degreased and connected to the positive pole of a direct-current generator. A platinum electrode (platinum coil, positive pole for electroanalytical metal deposition) was connected to the negative pole. The Ag electrode was then immersed to a depth of about 5-6 cm in 0.1 M HCl and electrolysed while stirring continuously with magnetic stirrer for about 1-2 hours at 1-2 mA to assure a uniform brown coating of silver chloride.

3.5 UV-Vis Spectroscopy Analysis Procedures

3.5.1 Preparation of 100 mg/L Chloride Stock Solution

5.00 ± 0.06 mL of 1000 mg/L of chloride standard solution was pipetted into a 50.00 ± 0.06 mL volumetric flask and topped up to the mark with deionized water.

3.5.2 Sample Preparation and Chloride Determination

1.000 ± 0.008 mL of acid copper sulfate sample solution, 1.5 mL of ethylene glycol and 1 mL of 0.1M $AgNO_3$ were pipetted into a 25 ± 0.04 mL volumetric flask. After topping up to the mark with deionized water, the sample solution was shaken vigorously. The same procedure was repeated to prepare the spiked sample solution (with 2.5, 5.0 and 7.5 mg/L of chloride). After storing in the dark for 5 minutes, all the sample solutions were measured against deionized water as the blank for absorbance at 470 nm immediately. In this standard addition method, the concentration of chloride was extrapolated via the negative intercept on x-axis from the calibration curve of absorbance versus concentration of chloride (taken into account of the dilution factor).

A total of 10 set of sample solutions were prepared and each solution was measured for three times.

3.5.3 Instrumentation

A double beam Perkin Elmer Lambda 25 UV-Vis system was used to perform all the measurements. The instrument's operating settings were shown in Table 3.3 below.

Table 3.3: Operating settings of Perkin Elmer Lambda 25 UV-Vis system

Parameter	Setting
Wavelength	470 nm
Slit wide	1 nm
Lamp change	326 nm
Ordinate mode	Absorption
Response	2 s

3.5.3.1 Warm Up of UV-Vis System

The UV-Vis spectrometer was switched on for at least 10 minutes before analysis to allow the lamps to warm up and stabilize. The UV Winlab was used to run the method and to explore the spectra obtained.

3.6 Ion Chromatography Analysis Procedures

3.6.1 Sample Preparation and Chloride Determination

Acid copper sulfate sample solution was diluted 1:100 in a 100 ± 0.1 mL volumetric flask with deionized water. The diluted sample solution was then poured into a sample vial and sealed with a filter cap after making sure that no air bubbles were trapped at the bottom. To prevent any contaminants from the vials and filter caps, they were rinsed thoroughly with deionized water, followed by the sample solution before being used and forceps were used to handle them. Before loading the vials into the sample carousel, any liquid trapped inside the cap socket was shaken off. The same procedure was repeated to prepare another three sample solutions which were spiked with 0.5, 1.0 and 1.5 mg/L of chloride respectively from the 1000 mg/L chloride standard solution. A total of 7 set of sample solutions were prepared and each solution was analyzed for three times in order to get a mean value. In this standard addition analysis, the concentration of chloride was extrapolated via the negative intercept on x-axis from the calibration curve of peak area versus concentration of the chloride added (taken into account of the dilution factor).

3.6.2 Instrumentation

The measurements were done using a Dionex ICS-5000 IC system consisting of SP-5 single pump, DC-5 conductivity detector, AS-DV autosampler, EG40 eluent generator, EGC-KOH cartridge, ASRS® 300 suppressor (4 mm), AS11-HC analytical column (4 x 250 mm), AG11-HC guard column (4 x 50 mm) and 25 µL of PEEK sample loop. The instrument's operating settings were shown in Table 3.4 below.

Table 3.4: Operating settings of Dionex ICS-5000 Ion Chromatography system

Parameter	Setting
Elution mode	Isocratic
Eluent	20 mM KOH
Flow rate	1.2 mL/min
Sample volume	25 µL
Delivery speed	4 mL/min
Run time	12 min
ASRS current setting	60 mA
Detection mode	Suppressed conductivity (recycle mode)
Compartment temperature	30 ^{o}C
Column temperature	30 ^{o}C

3.6.2.1 Start Up and Equilibration of Ion Chromatography system

Before the sample injection, the IC system was fully equilibrated and the background was completely stable for some time to ensure the accuracy and precision of the results. The pump was also primed for at least 5 minutes at a flow rate of 6 mL/min in order to remove any possible contaminants and air. The Smart Startup feature in Chromeleon software was used to automate the system start up and equilibration. It helps to monitor if the temperature of thermal compartments are at their set points, pump pressure is at the expected reading for the installed column (around 2200 psi) and detector baseline is at the expected reading for this application (around 1 µS) and stable.

CHAPTER 4

RESULTS AND DISCUSSION

4.1 Potentiometic Titration Result

In this method, the Ag electrode was coated with a thin uniform layer of AgCl to increase its resistance to the highly acidic acid copper sulfate plating solution and to improve its response to be faster and more stable. Without using any colour indicator, endpoints of either the titrations of acid copper sulfate plating solutions or NaCl standard solutions were determined potentiometrically with the coated Ag electrode. 0.01 M $AgNO_3$ volumetric solution was first standardized with standard NaCl solutions containing known amount of high purity NaCl. The results were tabulated in Table 4.1.

Table 4.1: Titer of 0.01 M $AgNO_3$ volumetric solution

Amount of NaCl weighed (g)	Replicate No.	Vol. of titrant used (mL)	Adjusted titer
0.00610	1	10.4579	0.9981
	2	10.4623	0.9977
	3	10.4598	0.9979
0.00612	1	10.4744	0.9998
	2	10.4684	1.0004
	3	10.8118	0.9971
0.00630	1	10.8005	0.9981
	2	10.8373	0.9947
	3	10.4728	1.0000
			Mean: 0.9982 ± 0.0013

The mean of the adjusted titer stored automatically in the system was then used to calculate the chloride content in the consequent titrations of acid copper sulfate plating solutions and the results were tabulated in Table 4.2.

Table 4.2: Concentration of chloride in acid copper sulfate plating solutions determined by potentiometric titration method

Replicate No.	Vol. of sample (mL)	Vol. of titrant used (mL)	Conc. of chloride (mg/L)
1	50	7.9893	56.54
2	50	7.9790	56.47
3	50	8.0088	56.66
4	50	7.9796	56.46
5	50	7.9740	56.42
6	50	7.9902	56.53
7	50	7.9839	56.49
8	50	7.9560	56.29
9	50	7.9827	56.48
10	50	7.9772	56.44
			Mean: 56.48 ± 0.07
			Standard deviation: 0.0945
			Relative standard deviation (%): 0.1673

The endpoint was indicated by the maximum of the red line which is the first derivative of the titration curve as shown in Figure 4.1. Between measurements, any white deposit of AgCl on the Ag electrode must be cleaned gently (care not to remove the coating) as this may decrease its response and lead to splitted peak as shown in Figure 4.2.

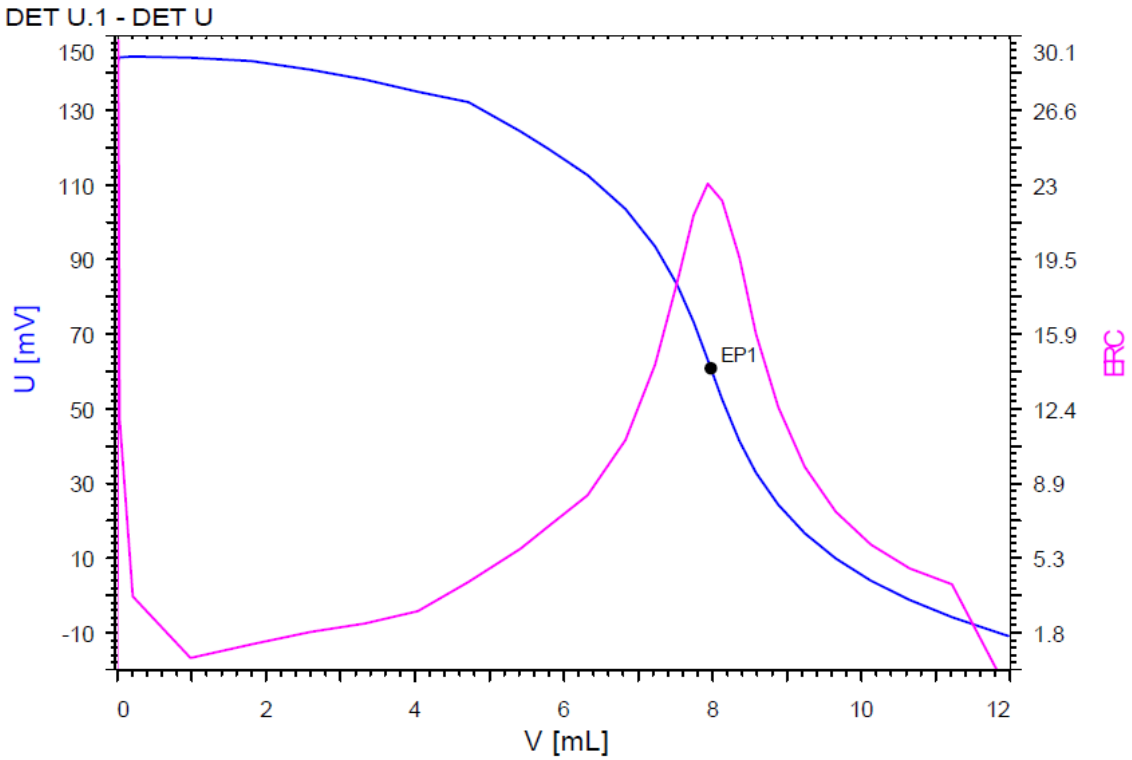


Figure 4.1: Typical potentiometric titration curve

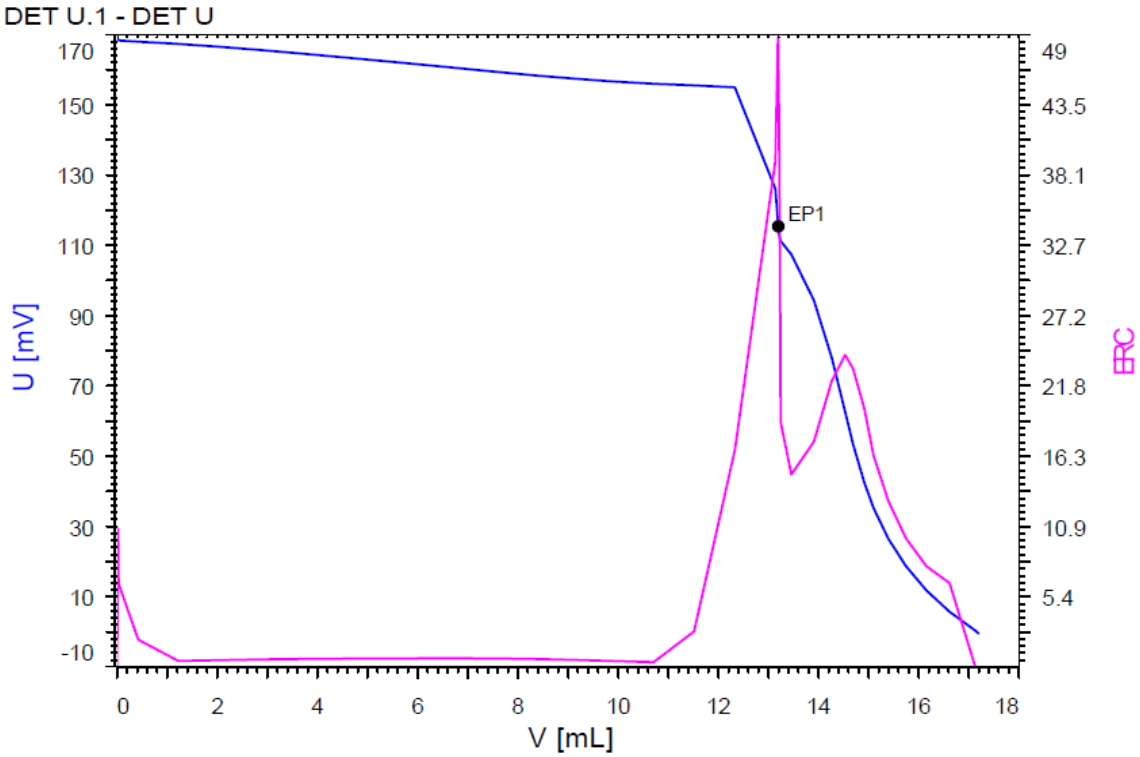


Figure 4.2: Potentiometric titration curve with splitted peak

In order to investigate the effect of potential contaminants on the accuracy and precision of this potentiometric titration method, 10 spiked sample were also determined using the same operating conditions and the results were shown in Table 4.3. By fixing the total sample volume used in each titration to 50 mL, spiking of 2.5 mL of 1000 mg/L of chloride standard solution into the 47.5 mL of the sample of acid copper sulfate plating solution gives the theoretical concentration of 103.65 mg/L. This value is then used to evaluate the recovery (%) that indicates the accuracy of the method. Recovery (%) was calculated by using the following equation:

$$\text{Recovery (\%)} = \frac{\text{Mean of measured value}}{\text{Theoretical value}} \times 100\%$$

Table 4.3: Concentration of chloride in spike acid copper sulfate plating solutions determined by potentiometric titration method

Replicate No.	Vol. of titrant used (mL)	Conc.of chloride (mg/L)	Recovery (%)
1	14.5345	102.83	99.21
2	14.4873	102.50	98.89
3	14.5566	102.99	99.36
4	14.5099	102.66	99.04
5	14.5517	102.95	99.32
6	14.5809	103.16	99.53
7	14.5694	103.08	99.45
8	14.5594	103.01	99.38
9	14.5471	102.92	99.30
10	14.5301	102.80	99.18
			Mean recovery (%): 99.27 ± 0.14
			Standard deviation: 0.1915
			Relative standard deviation (%): 0.1929

The achieved recovery is as high as 99.27 ± 0.14%. This suggests that the potentiometric titration method is very accurate, suffering little or no interference from the metal ion contaminants. On the other, this method also shows high precision as the relative standard deviation is only 0.1929%.

4.2 UV-Vis Spectroscopy Result

Chloride in the acid copper sulfate plating solution was determined photometrically by measuring the turbidity at 470 nm associated with the AgCl precipitates that form when chloride reacts with $AgNO_3$ as shown in Figure 4.3. A small amount of ethylene glycol which serves as a protective colloid was added into the sample solution to prevent the coagulation of the AgCl precipitates. The formation of AgCl colloids was facilitated by shaking the sample solution vigorously. The prepared sample solutions were then stored in the dark for 5 minutes to ensure complete reaction between chloride and $AgNO_3$. However, they must be measured as soon as possible because the AgCl precipitates will still eventually coagulate together, leading to measurement error. In order to eliminate the matrix interference, standard addition was employed. The concentration of chloride in the sample extrapolated from the negative intercept on x-axis from the standard addition curve as shown in Figure 4.4, taking the dilution factor (x25) into account. The respective results were tabulated in Table 4.4.

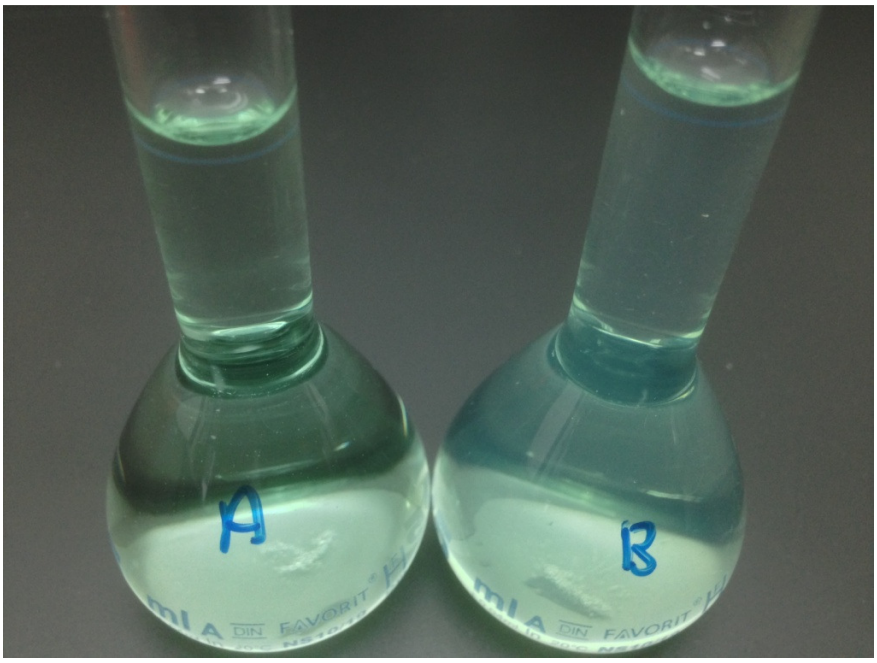


Figure 4.3: Sample solution before (A) and after (B) the addition of $AgNO_3$ solution

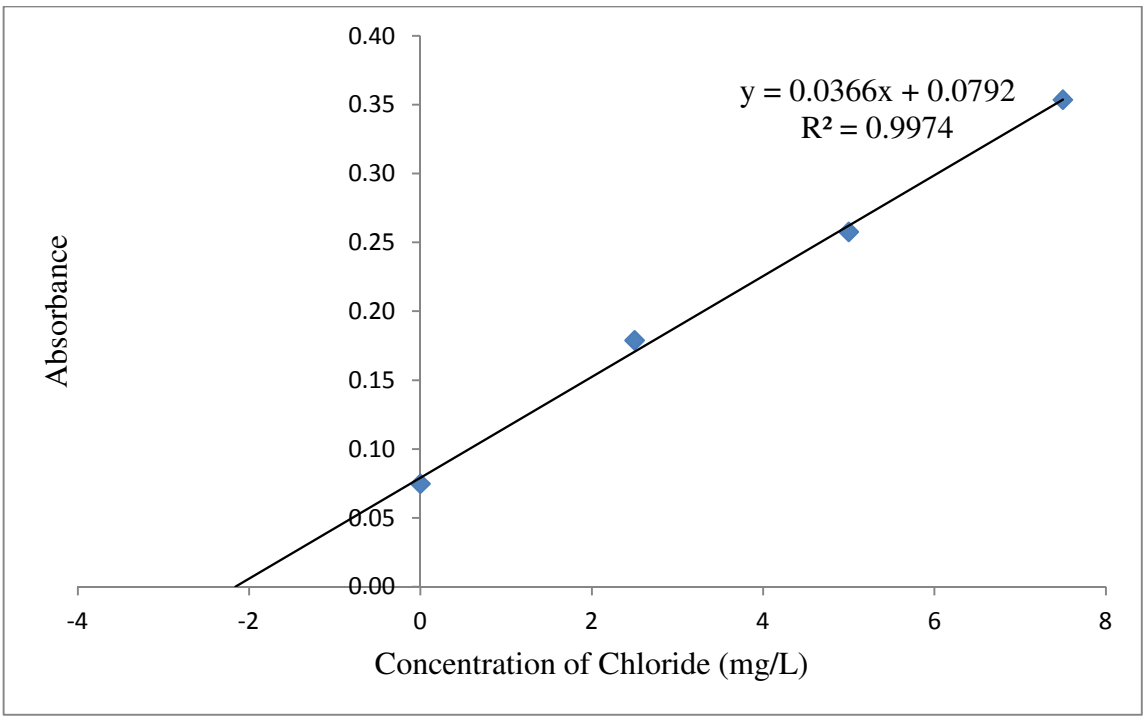


Figure 4.4: Typical standard addition curve

Table 4.4: Concentration of chloride in acid copper sulfate plating solutions determined by UV-Vis spectroscopy method

Replicate No.	Conc. of chloride (mg/L)	Recovery (%)
1	54.10	95.79
2	55.25	97.82
3	56.20	99.50
4	55.01	97.40
5	55.25	97.82
6	54.66	96.78
7	53.73	95.13
8	54.13	95.84
9	54.39	96.30
10	54.31	96.16
		Mean recovery (%): 96.85 ± 0.93
		Standard deviation: 1.2966
		Relative standard deviation (%): 1.3387

Since the potentiometric titration method discussed in the previous section demonstrates high accuracy and precision, the concentration of chloride found in the sample solution (56.48 mg/L) was used as the reference value to evaluate the spectroscopy recovery (%). From the result, it shows that UV-Vis spectroscopy method is also quite reliable, as the achieved recovery is as high as 96.85 ± 0.93% while the relative standard deviation is only 1.3387%.

4.3 Ion Chromatography Result

In this method, when acid copper sulfate sample solution passed through the anion exchange column, the trace amount of chlorides are separated from the other matrix components based on its affinity to the stationary phase. The eluted ions are then detected and quantified by a conductivity detector. The retention time of chloride was observed at around 3.75 ± 0.01 minutes as shown in Figure 4.5. However the retention time will decrease gradually due to the loss of column efficiency. All other uninterested peaks were removed by adjusting the detection criteria using Chromeleon software. Standard addition calibration method was also employed in this separation technique in order to eliminate the matrix interference. The concentration of chloride was extrapolated from the negative intercept on x-axis from the calibration curve of area of chloride peak versus concentration of chloride as shown in Figure 4.6 and the results were tabulated in Table 4.5.

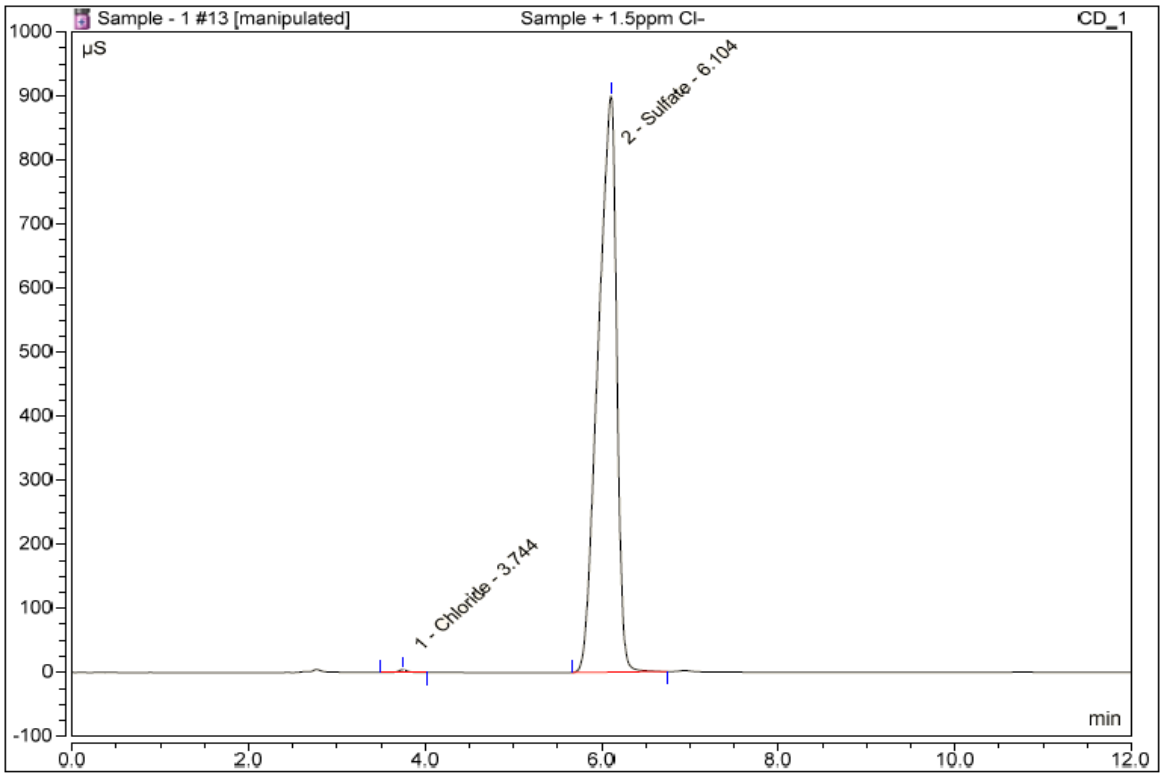


Figure 4.5: Ion chromatogram of acid copper sulfate sample solution spiked with 1.5 mg/L of chloride

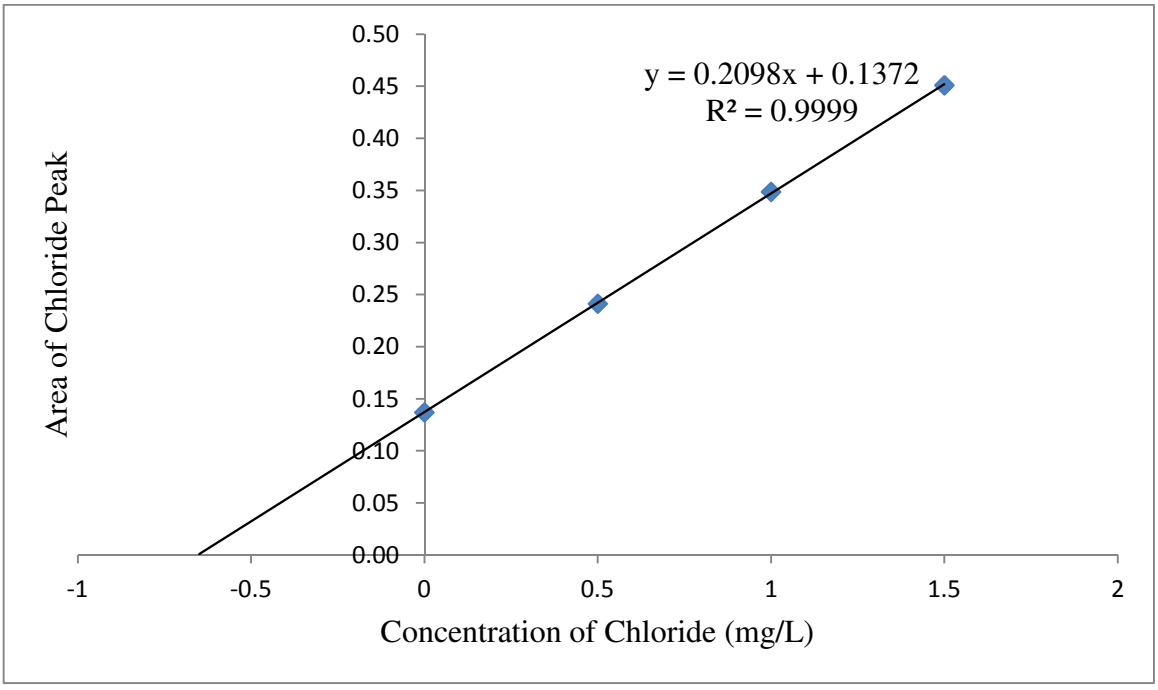


Figure 4.6: Calibration curve of area of chloride peak versus concentration of chloride (mg/L) of sample replicate no. 1

Table 4.5: Concentration of chloride in acid copper sulfate plating solutions determined by ion chromatography method

Replicate No.	Conc. of chloride (mg/L)	Recovery (%)
1	65.37	115.74
2	67.35	119.25
3	64.60	114.38
4	63.92	113.17
5	61.95	109.68
6	60.80	107.65
7	60.62	107.33
		Mean recovery (%): 112.46 ± 4.10
		Standard deviation: 4.4376
		Relative standard deviation (%): 3.9460

The recovery (%) of this IC method was also calculated based on the above mentioned reference value. As observed from the result, this method gave a positive determination error as much as 12.46% and poor precision with relative standard deviation as high as 3.9460% based on the results of 7 replicates. At first, 10 replicates were planned so that the results are readily comparable with those from previous methods without complicated statistical treatment. However, the column lost its efficiency so rapid throughout all these measurements until it was no longer able to separate the chloride peak from the nearby unknown peak as shown in Figure 4.7.

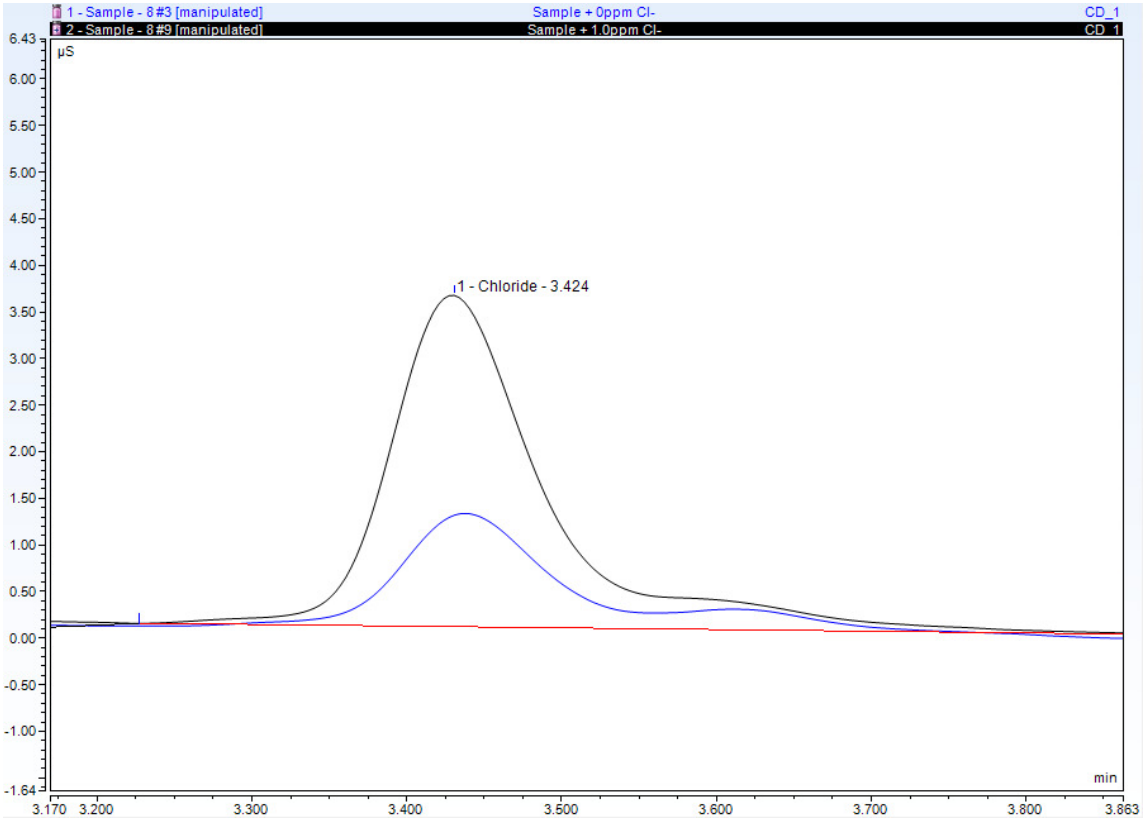


Figure 4.7: Enlarged ion chromatogram of unspiked (blue peak) and spiked (black peak) samples

4.4 Methods Comparison

In order to compare the results obtained by these three methods statistically, Oneway Anova (Table 4.6) and Tukey-Kramer test (Table 4.7) were conducted.

Table 4.6: Oneway Anova test

Oneway Anova (analysis of variance)					
Source	DF	Sum of squares	Mean square	F ratio	Prob > F
Method	2	341.42953	170.715	96.1820	< 0.001
Error	24	42.59794	1.775		
C. Total	26	384.02747			
Means for Oneway Anova					
Level	No.	Mean	Std Error	Lower 95%	Upper 95%
IC	7	63.52 ± 1.04	0.50355	62.476	64.555
Titration	10	56.48 ± 0.87	0.42130	55.608	57.348
UV-Vis	10	54.70 ± 0.87	0.42130	53.833	55.573

* A large F ratio indicates a great variation among group means

Table 4.7: Tukey-Kramer test

Abs (Dif)-HSD	IC	Titration	Uv-Vis
IC	-1.7784	5.3981	7.1731
Titration	5.3981	-1.4879	0.2871
UV-Vis	7.1731	0.2871	-1.4879

* Positive values show pairs of means that are significant different.

From these two tests, we can conclude that the results from these three methods are significant different. Among them, IC results showed the greatest different from the other two methods. In addition, from the Oneway analysis of chloride concentration by methods as illustrated in Figure 4.8, we can observe that potentiometric titration method has an excellent precision and accuracy, UV-Vis method is quite precise but less accurate, and IC method is the least precise and accurate.

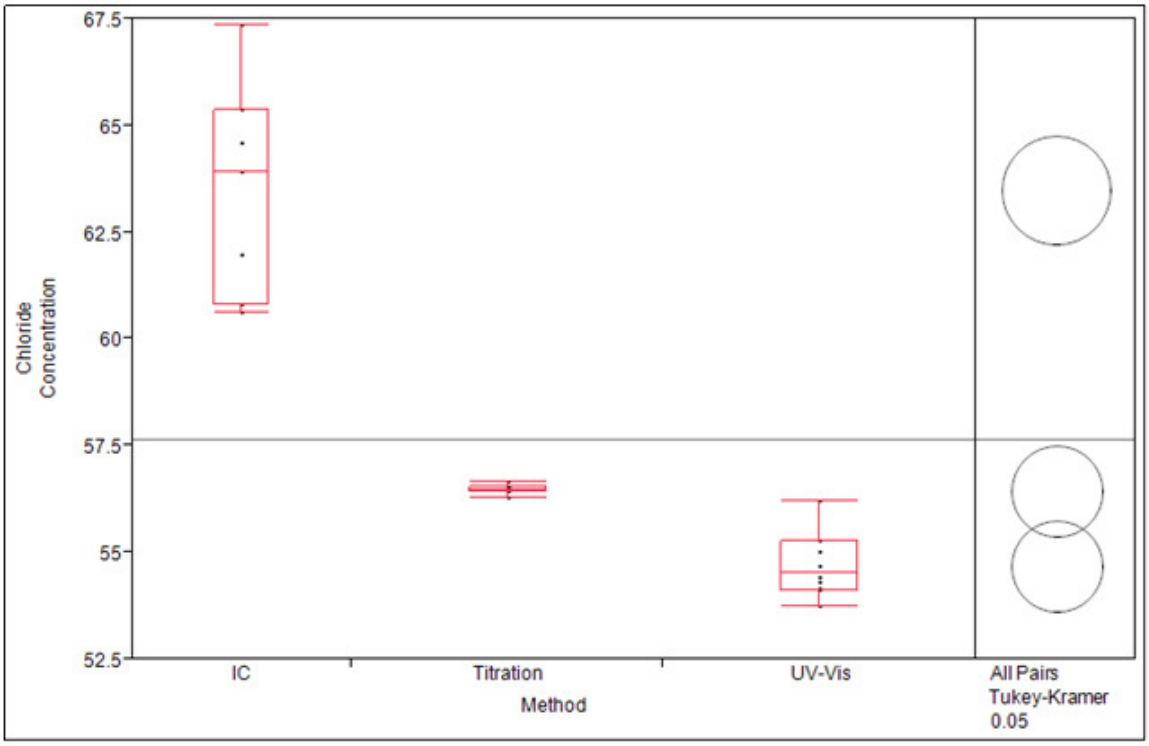


Figure 4.8: Oneway analysis of chloride concentration by methods

Undeniable that potentiometic titration is the best method for determination of chloride in acid copper sulfate plating bath among all three methods that were studied. The automation of the titration and replacement of colour indicators help to eliminate the possible human errors in conventional manual titration, thus greatly improve the measurement accuracy and precision. Furthermore, it was also verified with spiked samples to be free from potential interference by contaminants species, as capable in achieving an almost perfect recovery (%). In addition, this method is simple; does not require any tedious sample preparation steps or any other reagents, and fast; the analysis time required for each analysis is only approximately 5 minutes, making it an ideal method to be used for monitoring the chloride content during daily operation.

On the other hand, UV-Vis spectroscopy method is also capable to provide good accuracy with measurement error less than < 5% and good precision as well. However, it requires relatively more tedious sample preparation steps due to the use of standard addition calibration technique in order to eliminate the matrix interference and thus leading to a longer analysis time. Potential measurement error can arise from the coagulation of AgCl precipitates if the prepared sample solutions are left for too long. In this regard, the in-charge personnel must be trained to gain the necessary analytical skills so that they are able to complete the analysis in a short time frame. Since this method is so skill dependent, measurement replicate or verification using sample with known concentration are always recommended in order to increase the accuracy and precision. However, this will certainly increase the workload and analysis time, thus making it not really ideal method to be used in case of having a large amount of samples.

Lastly, IC method showed the poorest accuracy and precision among all methods. This error may be due to the existence of the much higher sulfate peak which lowers the sensitivity towards the trace amount of chloride (ppm level). By using this

method, it is necessary to prepare a set of calibration standards just like UV-Vis spectroscopy method, however it is easier, less skill dependent and requires no other reagents except the chloride standard solution. This means a lower reagent cost and man power, however it is definitely more expensive to maintain an ion chromatometer than an UV-Vis spectrometer, especially when the column efficiency depletes so fast due to the high salt content in the acid copper sulfate plating bath. Furthermore, it also have the longest analysis time as the measurement time required for one single injection only is more than 10 minutes, not including the time for sample preparation and system equilibration. On the other hand, it still offers some advantages such as the automation of sample injection which allows users to fully utilize it while reducing the workload and the simultaneous quantitation of sulfate content which is another major constituent in the acid copper sulfate plating bath besides of chloride, saving time. However, it seems that its disadvantages outweigh its advantages, making it the least suitable method to be used.

Table 4.8 below summarized the analytical performances of these three methods to ease the comparison.

Table 4.8: Analytical performances comparison among different methods

	Titration	UV-Vis	IC
Accuracy	High	Moderate	Low
Precision	High	Moderate	Low
Skill required	Low	High	Moderate
Reagents required	Little	Moderate	Little
Sample preparation time	Short	Long	Long
Analysis time	Short	Short	Long
Cost per sample	Low	Moderate	High
Maintenance Cost	Low	Low	High

CHAPTER 5

CONCLUSION

In this study, three different methods which include potentiometric titration, UV-Vis spectroscopy and IC were used to determine the chloride in an acid copper sulfate plating bath that had been used for a long time in order to investigate the effect of metallic ion contaminants on their analytical performances. As shown in the result, potentiometric titration method is the most accurate and precise method to be used, followed by UV-Vis spectroscopy and lastly IC method. Overall, matrix interference is no a serious issue in the evaluated methods. Potentiometric titration method demonstrated an almost prefect recovery percentage while standard addition technique was employed in UV-Vis spectroscopy and IC methods in order to eliminate this error as well. Comparable poor accuracy and precision of the IC method may be due to the decrease in sensitivity caused by the strong sulfate peak. For future study, analytical column with higher capacity can be used to get a better separation in peaks as well as sharper peak shape which in turn help to achieve a better signal to noise.

In term of ease to conduct, potentiometric titration method has the simplest sample preparation steps and does not require any other reagents. On the other hand, both UV-Vis spectroscopy and IC methods have more tedious sample preparations steps due to the use of standard addition technique, with the former method requires more reagents and is skill demanding. In term of analysis time, potentiometric titration method is the fastest, followed by UV-Vis spectroscopy and lastly IC method. In term of maintenance cost, again potentiometric titration method is the cheapest, followed by UV-Vis spectroscopy and lastly IC is the most expensive due to the fast depletion of column's efficiency. Considering all these factors, undoubtedly potentiometric titration

method is the most ideal method to be used to determine chloride in acid copper sulfate plating bath during daily operation for quick adjustment. Alternative methods such as UV-Vis spectroscopy and IC methods can be used in case of small sample quantity or for verification purposes.

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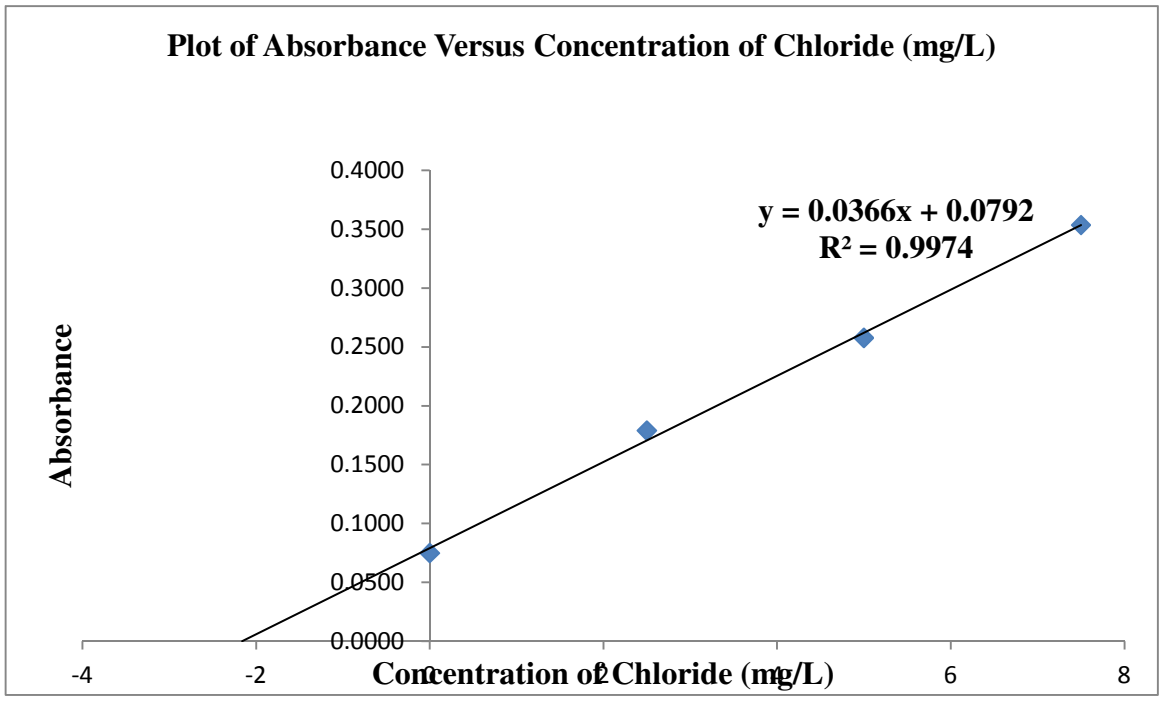
APPENDICES

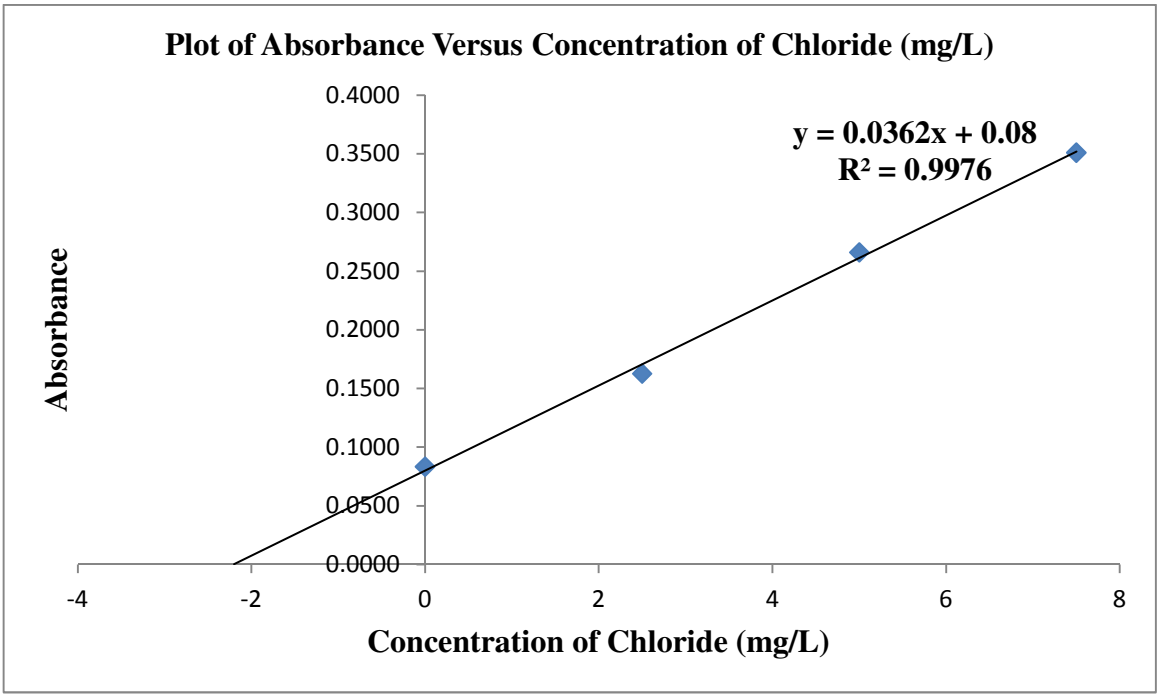
Appendix 1: Result and calibration curve for sample replicate no. 1 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0749	0.0750	0.0751	0.0750
2.5	0.1789	0.1790	0.1793	0.1791
5	0.2576	0.2578	0.2580	0.2578
7.5	0.3534	0.3532	0.3545	0.3537



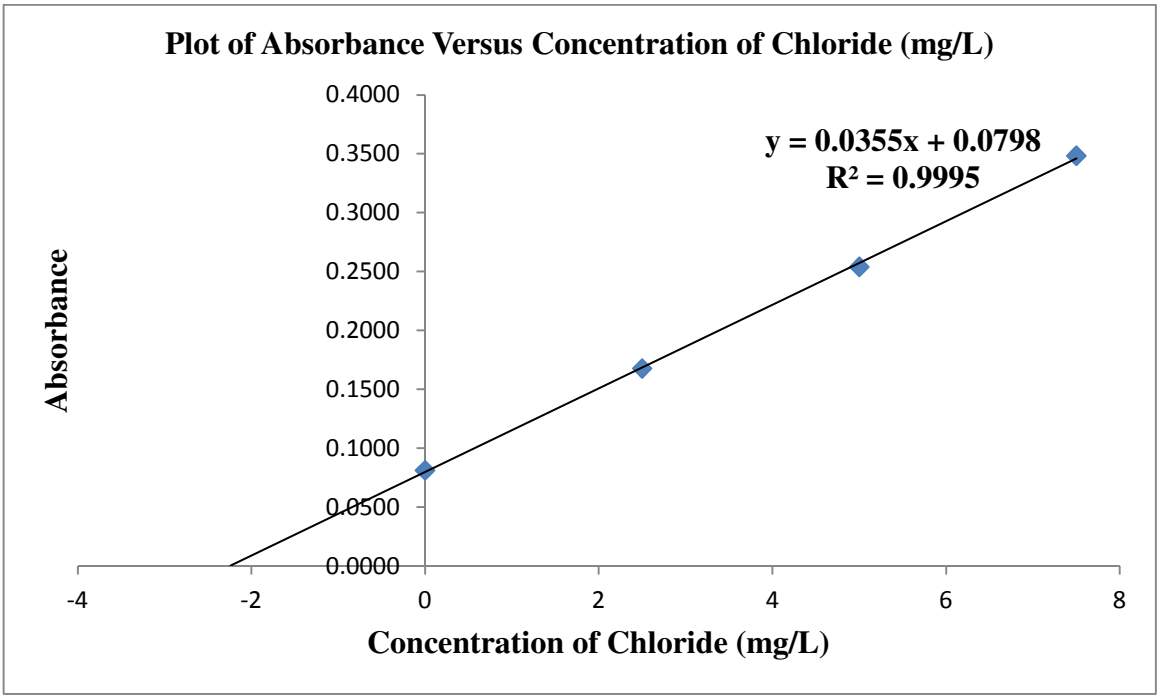
Appendix 2: Result and calibration curve for sample replicate no. 2 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0834	0.0835	0.0836	0.0835
2.5	0.1624	0.1628	0.1632	0.1628
5	0.2655	0.2662	0.2665	0.2661
7.5	0.3511	0.3509	0.3513	0.3511



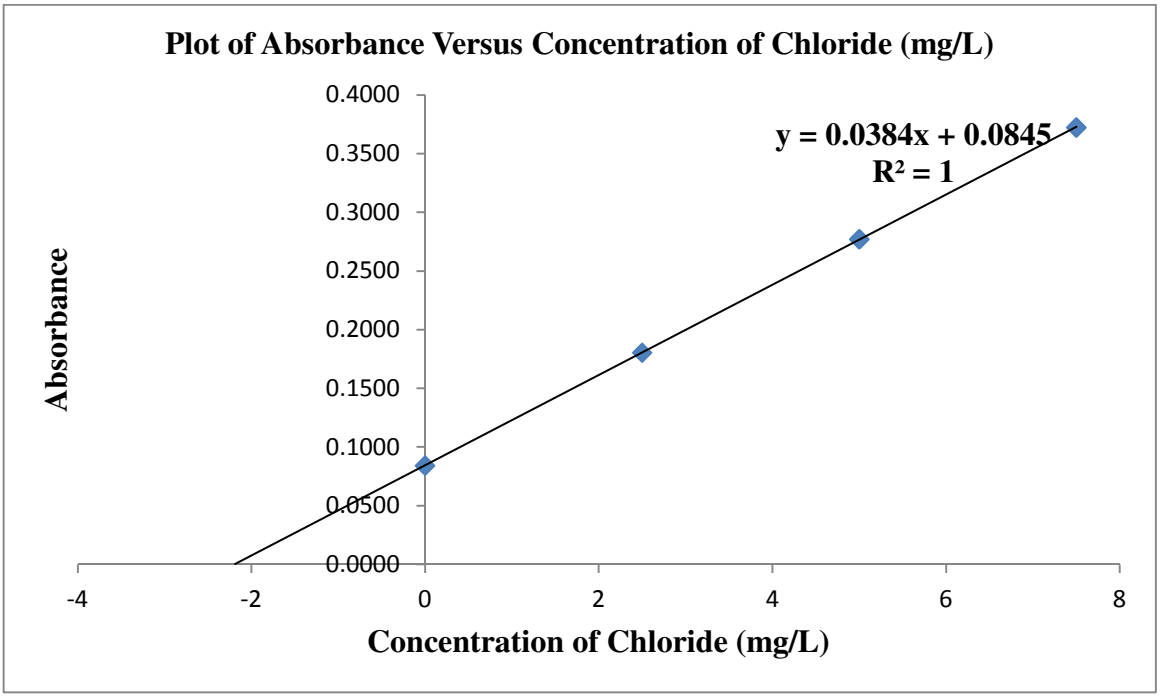
Appendix 3: Result and calibration curve for sample replicate no. 3 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0812	0.0815	0.0814	0.0814
2.5	0.1677	0.1678	0.1682	0.1679
5	0.254	0.2543	0.2543	0.2542
7.5	0.3482	0.3486	0.3488	0.3485



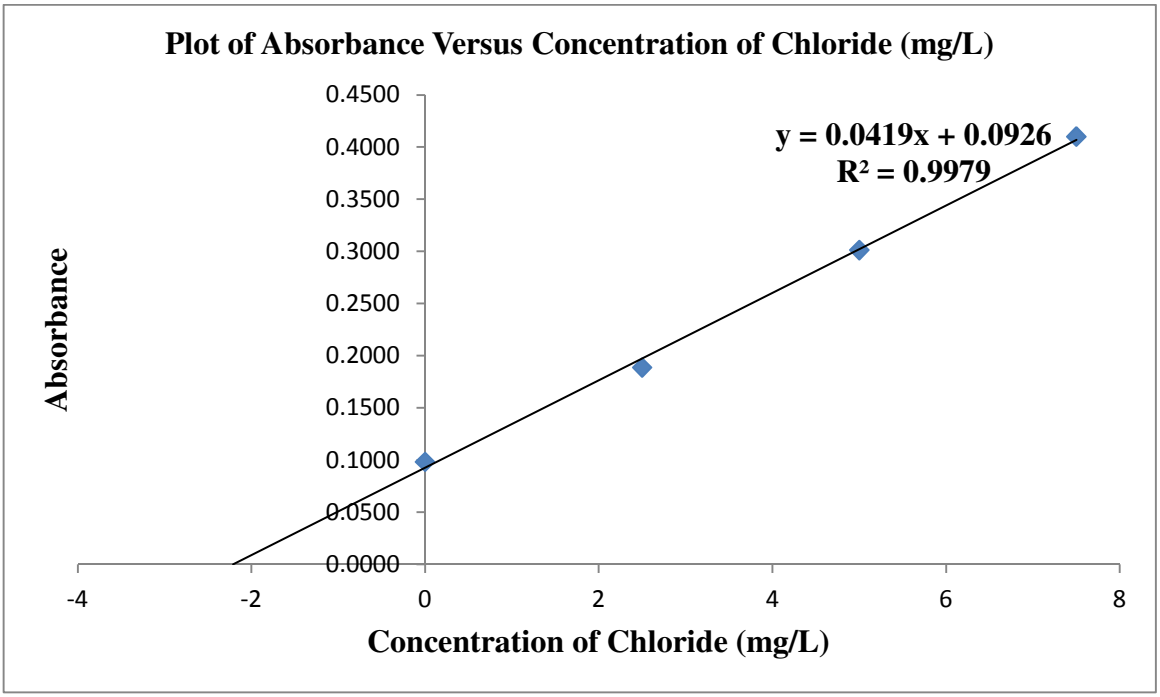
Appendix 4: Result and calibration curve for sample replicate no. 4 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0846	0.0842	0.0842	0.0843
2.5	0.1804	0.1805	0.1807	0.1805
5	0.2771	0.2772	0.2773	0.2772
7.5	0.3724	0.3723	0.3727	0.3725



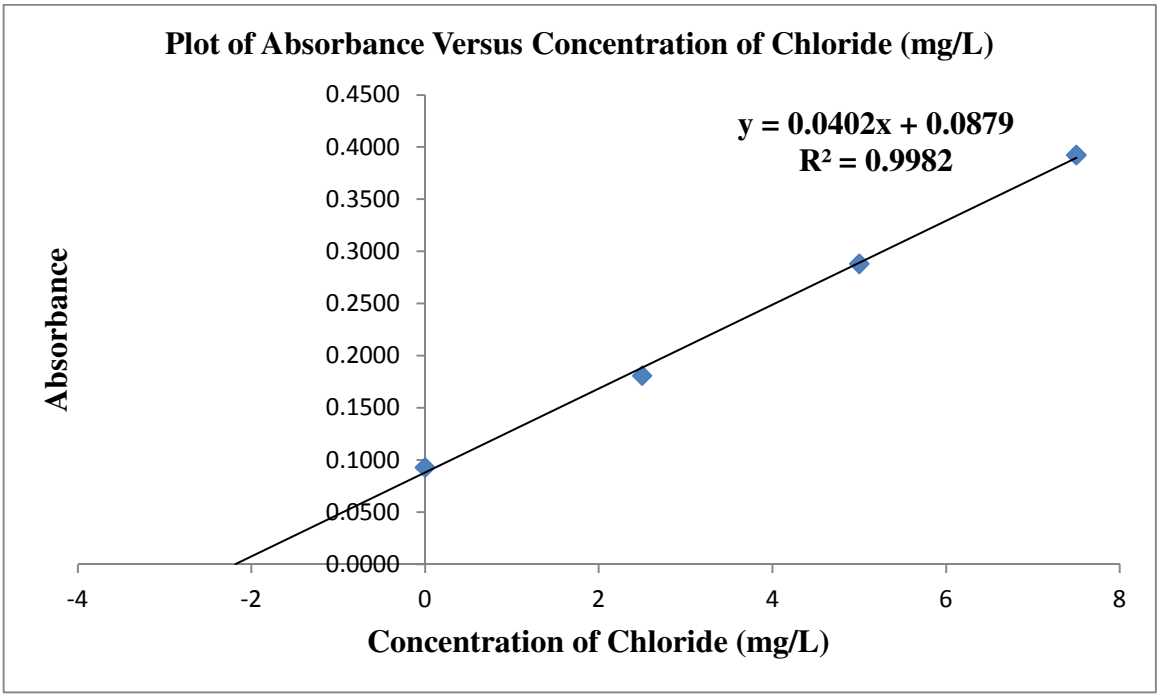
Appendix 5: Result and calibration curve for sample replicate no. 5 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0985	0.0985	0.0985	0.0985
2.5	0.1888	0.1891	0.189	0.1890
5	0.3013	0.3015	0.3018	0.3015
7.5	0.4099	0.4103	0.4106	0.4103



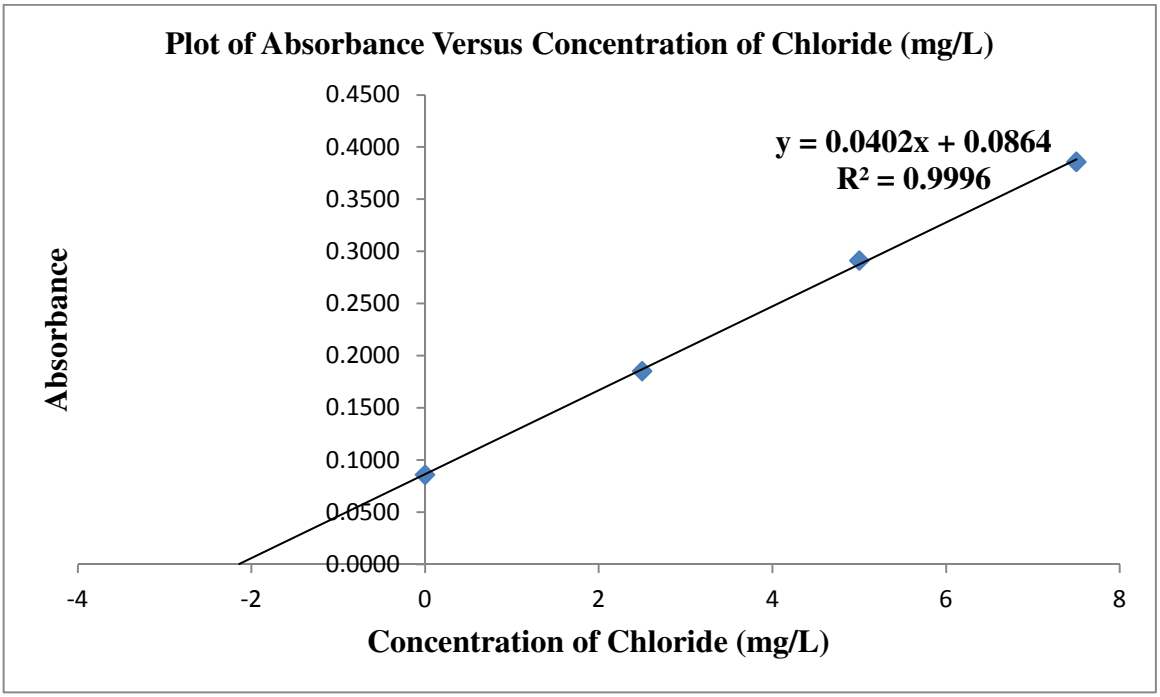
Appendix 6: Result and calibration curve for sample replicate no. 6 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.093	0.0931	0.0931	0.0931
2.5	0.1808	0.1811	0.1814	0.1811
5	0.2889	0.2881	0.2881	0.2884
7.5	0.3923	0.3924	0.3929	0.3925



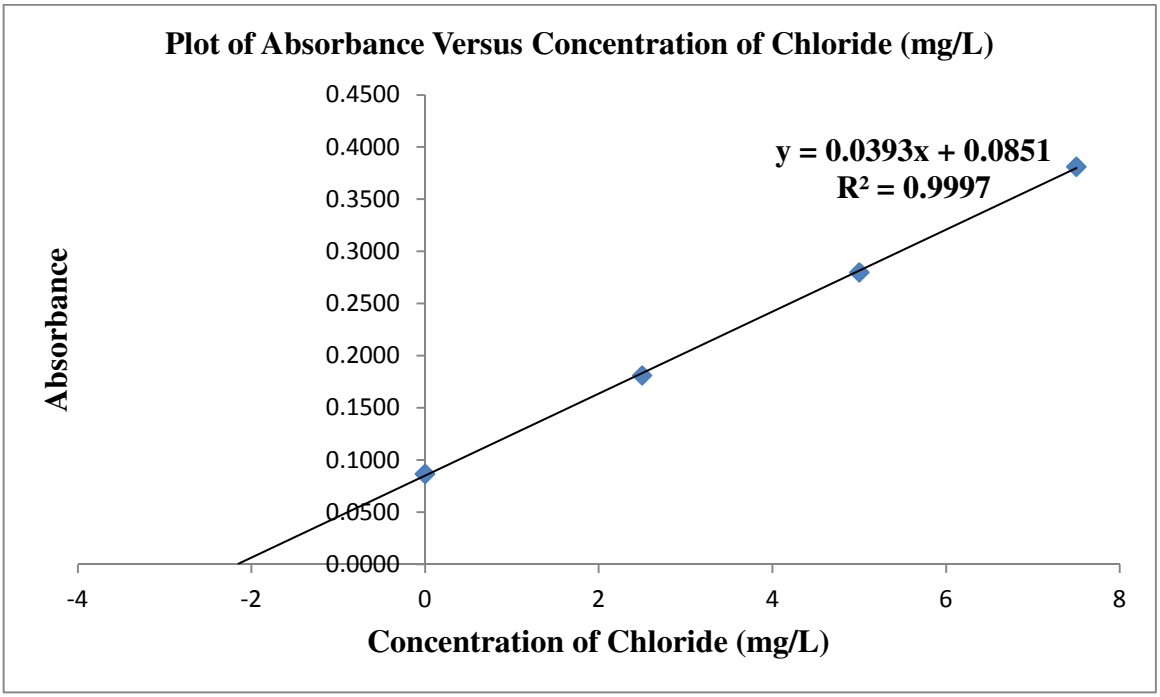
Appendix 7: Result and calibration curve for sample replicate no. 7 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0859	0.0862	0.0863	0.0861
2.5	0.185	0.1856	0.1858	0.1855
5	0.291	0.2916	0.2918	0.2915
7.5	0.3857	0.3861	0.3864	0.3861



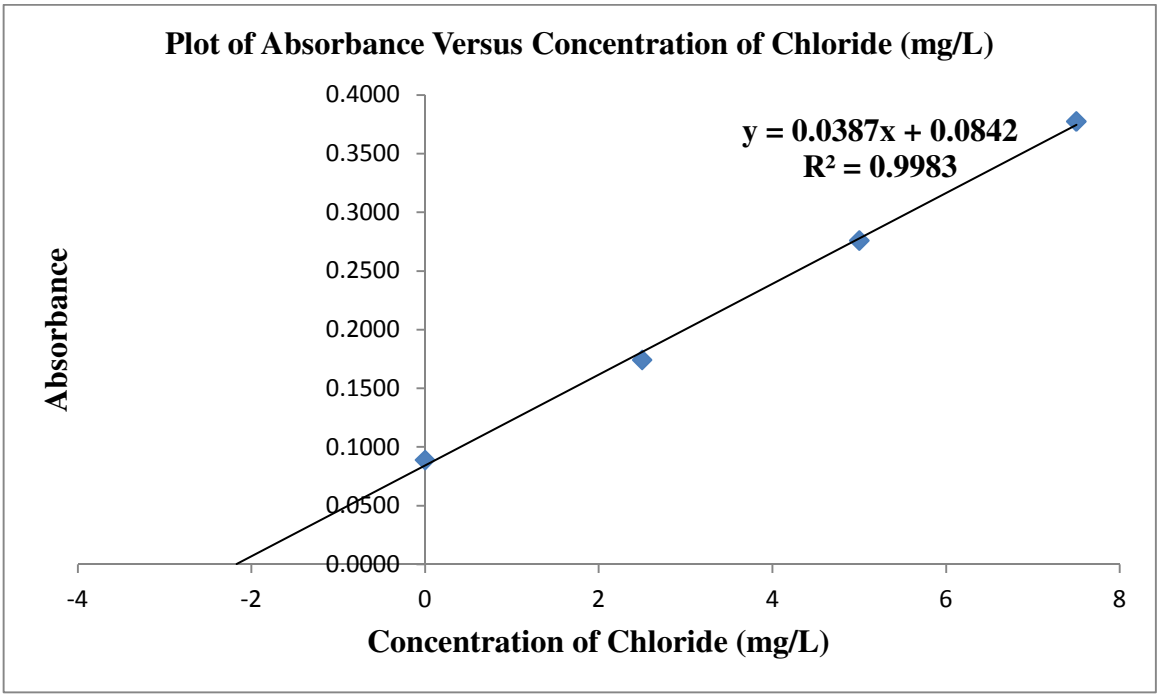
Appendix 8: Result and calibration curve for sample replicate no. 8 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0859	0.0862	0.0863	0.0861
2.5	0.185	0.1856	0.1858	0.1855
5	0.291	0.2916	0.2918	0.2915
7.5	0.3857	0.3861	0.3864	0.3861



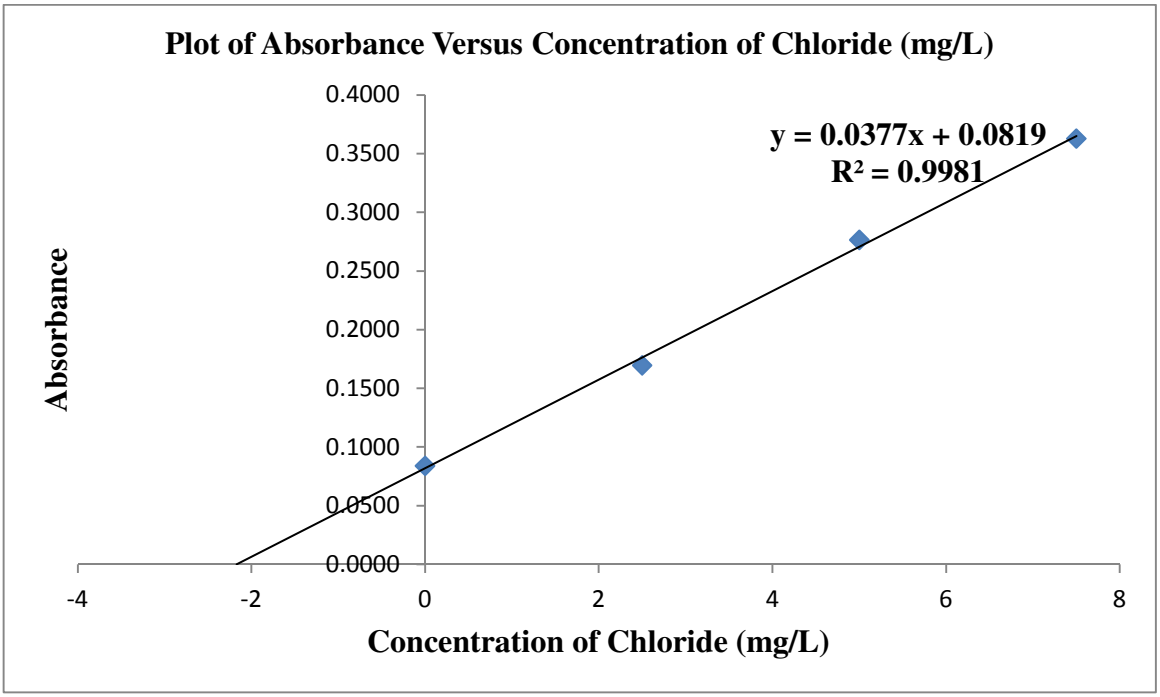
Appendix 9: Result and calibration curve for sample replicate no. 9 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0891	0.0892	0.0891	0.0891
2.5	0.1741	0.1744	0.1747	0.1744
5	0.2759	0.2761	0.2764	0.2761
7.5	0.3772	0.3777	0.378	0.3776



Appendix 10: Result and calibration curve for sample replicate no. 10 determined by UV-Vis method

Concentration of chloride (mg/L)	Absorbance			
	Scan 1	Scan 2	Scan 3	Average
0	0.0841	0.0842	0.0842	0.0842
2.5	0.1695	0.1699	0.1701	0.1698
5	0.2762	0.2767	0.277	0.2766
7.5	0.3625	0.3631	0.3634	0.3630

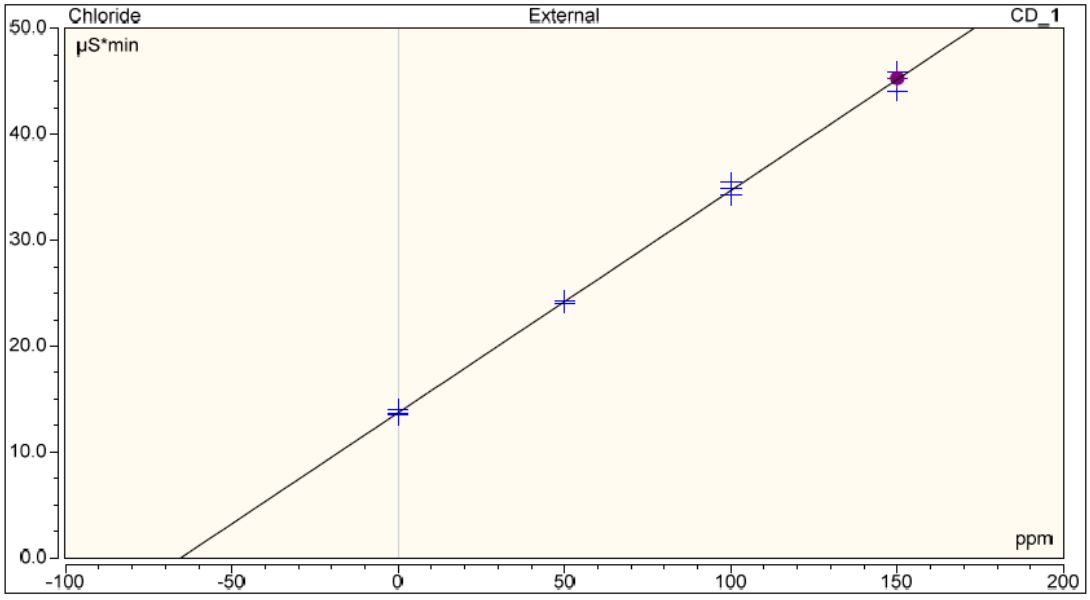


Appendix 11: Result and calibration curve for sample replicate no. 1 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.757	0.1406	0.07	1.15	0.13	66.9946
3	Sample + 0ppm Cl-	3.757	0.1348	0.06	1.13	0.13	64.2214
4	Sample + 0ppm Cl-	3.757	0.1361	0.06	1.16	0.13	64.8593
5	Sample + 0.5ppm Cl-	3.754	0.2409	0.11	2.12	0.24	64.7747
6	Sample + 0.5ppm Cl-	3.754	0.2402	0.11	2.12	0.24	64.4404
7	Sample + 0.5ppm Cl-	3.750	0.2432	0.11	2.16	0.24	65.8837
8	Sample + 1.0ppm Cl-	3.751	0.3426	0.16	3.13	0.35	63.2269
9	Sample + 1.0ppm Cl-	3.748	0.3548	0.16	3.22	0.36	69.0347
10	Sample + 1.0ppm Cl-	3.747	0.3489	0.16	3.18	0.35	66.2178
11	Sample + 1.5ppm Cl-	3.748	0.4595	0.21	4.17	0.46	68.9322
12	Sample + 1.5ppm Cl-	3.744	0.4407	0.20	4.14	0.46	59.9657
13	Sample + 1.5ppm Cl-	3.744	0.4531	0.21	4.20	0.46	65.9001
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	45.010	3.535	1.637	31.889	3.567	784.451
	Average:	3.751	0.295	0.136	2.657	0.297	65.371
	Rel.Std.Dev:	0.135 %	41.620 %	40.692 %	44.449 %	43.505 %	3.765 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	13.717	0.210	0.000	99.8226
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				13.7172	0.2099	0.0000	99.8226

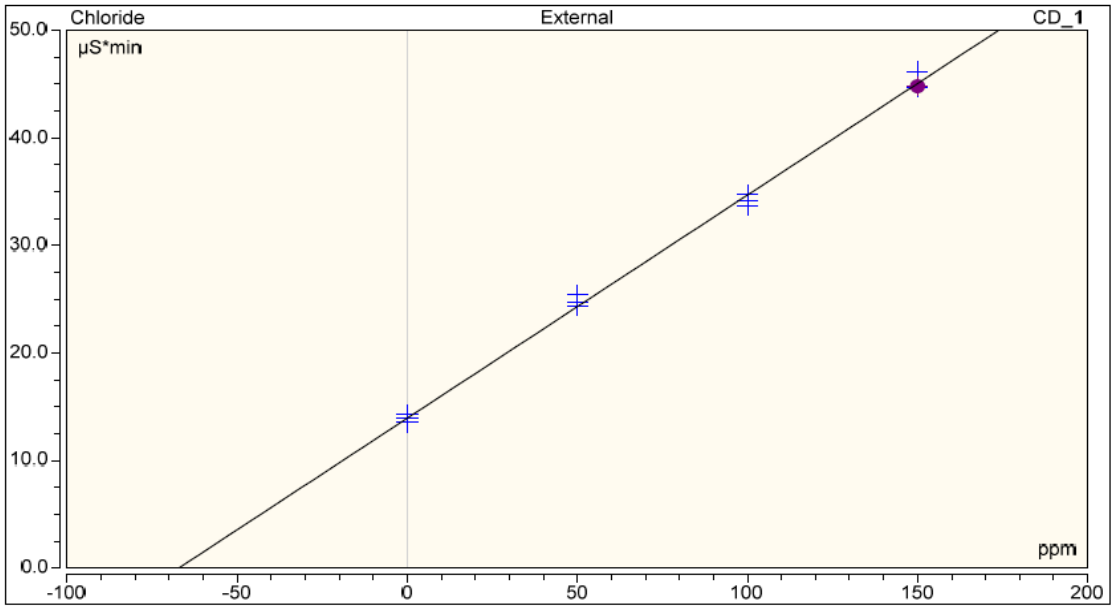


Appendix 12: Result and calibration curve for sample replicate no. 2 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.647	0.1394	0.06	1.19	0.13	67.1718
3	Sample + 0ppm Cl-	3.644	0.1432	0.06	1.20	0.13	69.0030
4	Sample + 0ppm Cl-	3.641	0.1354	0.06	1.17	0.13	65.2303
5	Sample + 0.5ppm Cl-	3.641	0.2471	0.11	2.26	0.25	69.0414
6	Sample + 0.5ppm Cl-	3.640	0.2539	0.11	2.32	0.25	72.3263
7	Sample + 0.5ppm Cl-	3.638	0.2438	0.11	2.25	0.24	67.4775
8	Sample + 1.0ppm Cl-	3.637	0.3372	0.15	3.22	0.35	62.4545
9	Sample + 1.0ppm Cl-	3.634	0.3413	0.15	3.23	0.35	64.4310
10	Sample + 1.0ppm Cl-	3.634	0.3472	0.15	3.26	0.35	67.2911
11	Sample + 1.5ppm Cl-	3.631	0.4619	0.20	4.33	0.47	72.5557
12	Sample + 1.5ppm Cl-	3.631	0.4468	0.19	4.27	0.46	65.2684
13	Sample + 1.5ppm Cl-	3.631	0.4481	0.19	4.30	0.46	65.9199
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	43.647	3.545	1.538	32.999	3.558	808.171
	Average:	3.637	0.295	0.128	2.750	0.297	67.348
	Rel.Std.Dev:	0.150 %	40.863 %	40.520 %	43.726 %	43.400 %	4.496 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	13.934	0.208	0.000	99.7275
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				13.9339	0.2075	0.0000	99.7275

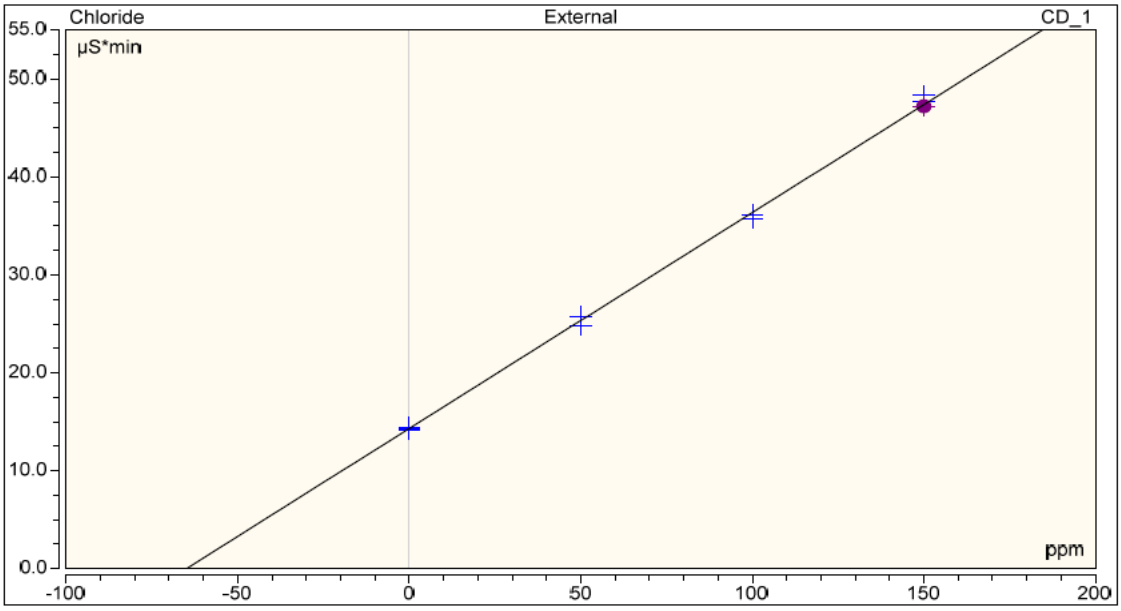


Appendix 13: Result and calibration curve for sample replicate no. 3 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.624	0.1448	0.06	1.23	0.13	65.6739
3	Sample + 0ppm Cl-	3.621	0.1431	0.06	1.21	0.13	64.9406
4	Sample + 0ppm Cl-	3.621	0.1415	0.06	1.23	0.13	64.1957
5	Sample + 0.5ppm Cl-	3.617	0.2480	0.11	2.29	0.24	62.5062
6	Sample + 0.5ppm Cl-	3.617	0.2577	0.11	2.32	0.25	66.9306
7	Sample + 0.5ppm Cl-	3.617	0.2480	0.11	2.30	0.24	62.5006
8	Sample + 1.0ppm Cl-	3.617	0.3577	0.15	3.39	0.36	62.2952
9	Sample + 1.0ppm Cl-	3.614	0.3572	0.15	3.40	0.36	62.0781
10	Sample + 1.0ppm Cl-	3.614	0.3617	0.15	3.41	0.36	64.1174
11	Sample + 1.5ppm Cl-	3.610	0.4766	0.20	4.51	0.48	66.2466
12	Sample + 1.5ppm Cl-	3.614	0.4838	0.21	4.55	0.48	69.5105
13	Sample + 1.5ppm Cl-	3.611	0.4722	0.20	4.51	0.48	64.2238
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	43.394	3.692	1.572	34.341	3.659	775.219
	Average:	3.616	0.308	0.131	2.862	0.305	64.602
	Rel.Std.Dev:	0.113 %	42.190 %	42.048 %	44.902 %	44.679 %	3.446 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	14.313	0.220	0.000	99.8536
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				14.3126	0.2204	0.0000	99.8536

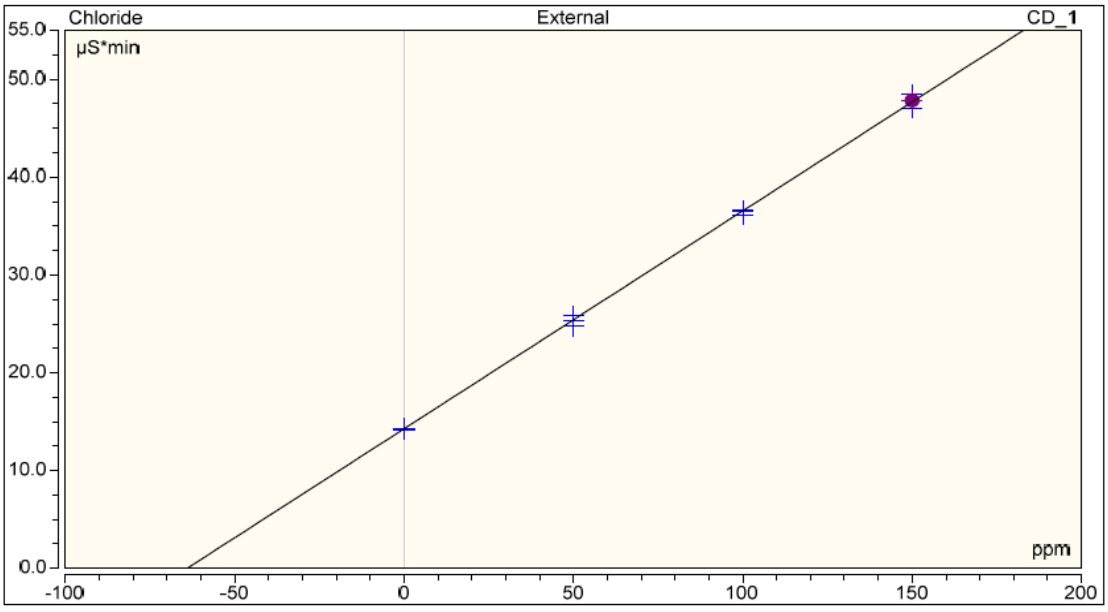


Appendix 14: Result and calibration curve for sample replicate no. 4 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.608	0.1426	0.06	1.22	0.13	64.0050
3	Sample + 0ppm Cl-	3.607	0.1434	0.06	1.23	0.13	64.3631
4	Sample + 0ppm Cl-	3.604	0.1420	0.06	1.24	0.13	63.7379
5	Sample + 0.5ppm Cl-	3.604	0.2538	0.11	2.31	0.25	63.8948
6	Sample + 0.5ppm Cl-	3.600	0.2475	0.10	2.29	0.24	61.0690
7	Sample + 0.5ppm Cl-	3.601	0.2586	0.11	2.33	0.25	66.0329
8	Sample + 1.0ppm Cl-	3.600	0.3610	0.15	3.43	0.36	61.9958
9	Sample + 1.0ppm Cl-	3.598	0.3659	0.15	3.46	0.37	64.1915
10	Sample + 1.0ppm Cl-	3.597	0.3656	0.15	3.47	0.37	64.0953
11	Sample + 1.5ppm Cl-	3.597	0.4709	0.20	4.52	0.48	61.3492
12	Sample + 1.5ppm Cl-	3.590	0.4849	0.20	4.56	0.48	67.6324
13	Sample + 1.5ppm Cl-	3.594	0.4784	0.20	4.57	0.48	64.7098
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	43.200	3.715	1.570	34.625	3.671	767.077
	Average:	3.600	0.310	0.131	2.885	0.306	63.923
	Rel.Std.Dev:	0.143 %	42.163 %	42.141 %	44.901 %	44.794 %	2.894 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	14.269	0.223	0.000	99.8998
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				14.2688	0.2228	0.0000	99.8998

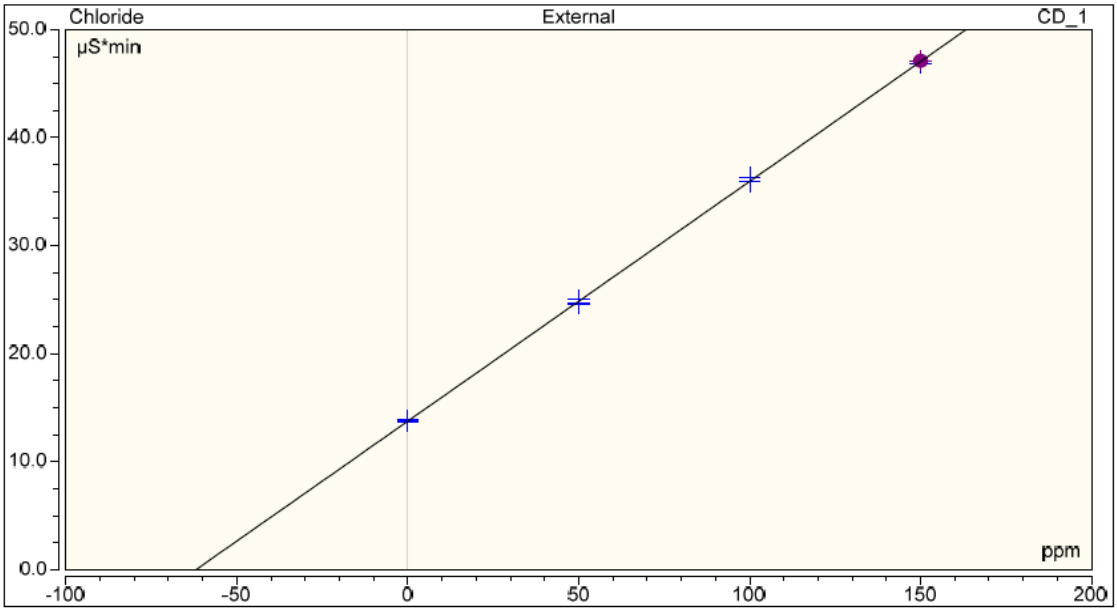


Appendix 15: Result and calibration curve for sample replicate no. 5 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.537	0.1368	0.06	1.22	0.13	61.6577
3	Sample + 0ppm Cl-	3.540	0.1385	0.06	1.24	0.13	62.4010
4	Sample + 0ppm Cl-	3.541	0.1374	0.06	1.23	0.13	61.9301
5	Sample + 0.5ppm Cl-	3.537	0.2502	0.10	2.36	0.25	62.7303
6	Sample + 0.5ppm Cl-	3.534	0.2466	0.10	2.35	0.25	61.1301
7	Sample + 0.5ppm Cl-	3.531	0.2457	0.10	2.33	0.25	60.7236
8	Sample + 1.0ppm Cl-	3.531	0.3588	0.15	3.48	0.37	61.6923
9	Sample + 1.0ppm Cl-	3.531	0.3635	0.15	3.49	0.37	63.8048
10	Sample + 1.0ppm Cl-	3.530	0.3590	0.15	3.50	0.37	61.7600
11	Sample + 1.5ppm Cl-	3.530	0.4690	0.20	4.61	0.49	61.3321
12	Sample + 1.5ppm Cl-	3.524	0.4704	0.20	4.62	0.49	61.9720
13	Sample + 1.5ppm Cl-	3.524	0.4712	0.20	4.64	0.49	62.3075
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	42.389	3.647	1.518	35.064	3.718	743.441
	Average:	3.532	0.304	0.127	2.922	0.310	61.953
	Rel.Std.Dev:	0.157 %	42.681 %	42.551 %	45.304 %	45.188 %	1.299 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	13.758	0.222	0.000	99.9810
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				13.7583	0.2219	0.0000	99.9810

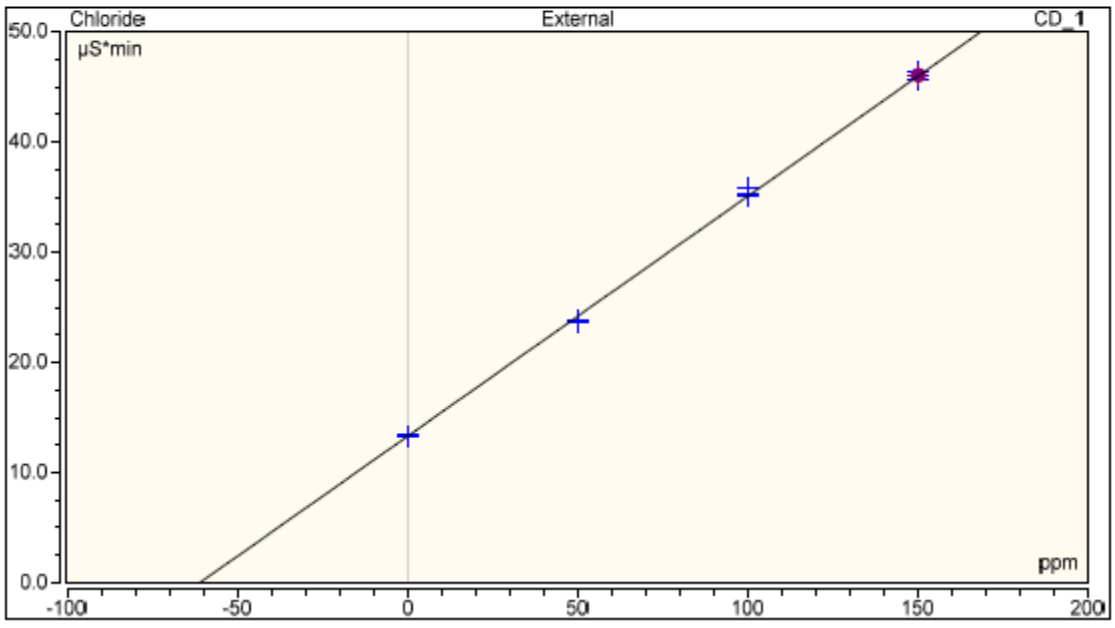


Appendix 16: Result and calibration curve for sample replicate no. 6 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.504	0.1332	0.06	1.21	0.13	61.1515
3	Sample + 0ppm Cl-	3.504	0.1323	0.06	1.23	0.13	60.7281
4	Sample + 0ppm Cl-	3.500	0.1339	0.06	1.23	0.13	61.4497
5	Sample + 0.5ppm Cl-	3.500	0.2379	0.10	2.34	0.25	59.1741
6	Sample + 0.5ppm Cl-	3.501	0.2358	0.10	2.31	0.25	58.2070
7	Sample + 0.5ppm Cl-	3.497	0.2368	0.10	2.33	0.25	58.6541
8	Sample + 1.0ppm Cl-	3.497	0.3581	0.15	3.50	0.37	64.3485
9	Sample + 1.0ppm Cl-	3.494	0.3502	0.14	3.47	0.37	60.7320
10	Sample + 1.0ppm Cl-	3.494	0.3526	0.15	3.48	0.37	61.8228
11	Sample + 1.5ppm Cl-	3.497	0.4561	0.19	4.58	0.49	59.3314
12	Sample + 1.5ppm Cl-	3.491	0.4632	0.19	4.61	0.49	62.5875
13	Sample + 1.5ppm Cl-	3.494	0.4608	0.19	4.60	0.49	61.4593
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	41.972	3.551	1.472	34.897	3.705	729.646
	Average:	3.498	0.296	0.123	2.908	0.309	60.804
	Rel.Std.Dev:	0.121 %	43.328 %	43.196 %	45.262 %	45.125 %	2.889 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	13.315	0.218	0.000	99.9079
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
		AVERAGE:		13.3154	0.2179	0.0000	99.9079



Appendix 17: Result and calibration curve for sample replicate no. 7 determined by IC method

No. Chloride	Name Chloride	Time min Chloride CD_1	Area µS*min Chloride CD_1	Rel.Area % Chloride CD_1	Height µS Chloride CD_1	Rel.Height % Chloride CD_1	Amount ppm Chloride CD_1
1	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
2	Sample + 0ppm Cl-	3.491	0.1277	0.05	1.20	0.13	59.7285
3	Sample + 0ppm Cl-	3.491	0.1314	0.05	1.20	0.13	61.4275
4	Sample + 0ppm Cl-	3.487	0.1302	0.05	1.21	0.13	60.8959
5	Sample + 0.5ppm Cl-	3.484	0.2357	0.10	2.33	0.25	60.2333
6	Sample + 0.5ppm Cl-	3.484	0.2382	0.10	2.34	0.25	61.3808
7	Sample + 0.5ppm Cl-	3.484	0.2355	0.10	2.27	0.24	60.1113
8	Sample + 1.0ppm Cl-	3.484	0.3420	0.14	3.42	0.36	59.9468
9	Sample + 1.0ppm Cl-	3.480	0.3439	0.14	3.44	0.36	60.8255
10	Sample + 1.0ppm Cl-	3.480	0.3411	0.14	3.43	0.36	59.5119
11	Sample + 1.5ppm Cl-	3.481	0.4533	0.19	4.58	0.49	61.9697
12	Sample + 1.5ppm Cl-	3.480	0.4516	0.19	4.57	0.48	61.1785
13	Sample + 1.5ppm Cl-	3.478	0.4495	0.19	4.56	0.48	60.1910
14	Water	n.a.	n.a.	n.a.	n.a.	n.a.	n.a.
	Sum:	41.802	3.480	1.437	34.559	3.666	727.401
	Average:	3.484	0.290	0.120	2.880	0.305	60.617
	Rel.Std.Dev:	0.118 %	43.126 %	43.030 %	45.479 %	45.357 %	1.273 %

Calibration Summary

Peak Name	Eval.Type	Cal.Type	Points	Offset (C0)	Slope (C1)	Curve (C2)	Coeff.Det. %
Chloride	Area	Lin	12.000	12.977	0.214	0.000	99.9824
Sulfate	Area	Lin	12.000	n.a.	n.a.	n.a.	n.a.
AVERAGE:				12.9766	0.2138	0.0000	99.9824